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THE Fe–Ni–S SYSTEM.[1]

AN INTRODUCTION WITH NEW DATA ON THE CRYSTALLIZATION OF PYRRHOTITE AND PENTLANDITE.

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ABSTRACT.

Mineralogic problems involved in the Fe–Ni–S System are listed and a critical review of both mineralogic and metallurgical data on the system is given. New experimental data obtained from melts of FeS and NiS are presented together with results of an experiment to test the immiscibility of these sulphides. For low-sulphur, iron-nickel melts confirmation is obtained that FeS (pyrrhotite) enters into a peritectic reaction with a nickel-rich liquid to form a ternary solid solution which on final cooling is equivalent to pentlandite. Though natural pentlandite appears to have a constant composition $(Fe, Ni)_9S_8$ with Fe : Ni = 10 : 11, synthetic pentlandites have been prepared from melts ranging in composition in one series of experiments from 45FeS–55NiS to 10FeS–90NiS. In another series, with probably lower sulphur, a compound, close to 30FeS–70NiS, approximating the compound $(FeS)_2Ni_5S_3$ (in Fe : Ni) and indistinguishable from pentlandite by x-ray methods, was obtained. Cooling curve data suggest that while the peritectic type of crystallization may occur with low sulphur, a solid solution series between iron and nickel sulphides may form over a still wider range. Confirmation of this will be presented in a later paper by Colgrove.

The textural relations of natural pyrrhotite and pentlandite are reviewed and new evidence for a natural, nickeliferous-pyrrhotite solid solution given. On the basis of studies of natural ores and experimental data, the mode of crystallization of non-aqueous, iron-nickel, sulphide liquids is traced and the importance of sulphur content stressed. No evidence is found that such sulphide liquids are immiscible.

[1] Experimental work which forms the basis of this paper was carried out by H. F. Zurbrigg, in 1933, and by G. L. Colgrove in 1939–1940, both of whom were graduate students at Queen's University in the years mentioned.

[2] Part of the investigation of this system was carried out with the aid of a bursary granted by The National Research Council of Canada to G. L. Colgrove, 1939–1940.

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INTRODUCTION.

MANY interesting problems arise in connection with the variations in composition and the relations existing between the several iron and nickel sulphides of mineral deposits which fall within the iron-nickel-sulphur system in composition. With hope of obtaining further data on some of these, particularly with regard to the solubility of nickel in pyrrhotite and the variation in composition of the mineral pentlandite, experiments were begun on the synthesis of iron and nickel sulphides of composition approximating and beyond that of some natural ores.

Two series of investigations were carried out at Queen's University in 1933 and 1939. A third, more complete series of experiments has been undertaken by G. L. Colgrove at the University of Wisconsin under the direction of Dr. R. C. Emmons. The earlier work formed a basis for the later, indicating the general direction which further research should follow, and is described. A critical survey of the geologic and mineralogic literature bearing on the subject, and a review of the results obtained by various metallurgists who have investigated that part of the system covered by Fe-Ni-FeS-Ni_3S_2 and Ni_6S_5 are included.

Minerals whose composition falls within this ternary system are pyrite, bravoite and other nickel-bearing pyrites, marcasite and nickeliferous marcasite, troilite, pyrrhotite, pentlandite, millerite and other crystal phases of NiS, violarite, polydymite, as well as iron-nickel alloys of meteors. Other compounds known to occur in the system but not described as minerals include Ni_3S_2, Ni_6S_5, NiS_2 and a ternary compound $2FeS.Ni_3S_2$. Still others have been suggested but have not been confirmed.

STATEMENT OF THE MINERALOGIC PROBLEMS.

Students of iron and nickel sulphide ores and the rather voluminous literature concerning them are familiar with the difficulties of ascertaining the paragenesis of such ores and the exact composition of their components. Problems involved in ores of

this type, although only some of the more outstanding are included in this study, may be classified as follows:

I. Composition of Minerals in the Fe-Ni-S System.
   1. The limits of solid solution of nickel in pyrite. Studies of this are to be given in a later paper by Colgrove.
   2. The solubility of nickel in pyrrhotites.
   3. The question whether the compound pentlandite may exist as a solid solution series and if so, the limits of its variation in composition.
   4. Variation in sulphur content of the different iron, iron-nickel and nickel sulphides and its influence on the type of substance formed. Nickel-bearing marcasite has not been included in these studies.

II. Crystal Phases of the Compounds and Solid Solutions.
   1. Pyrrhotites—FeS_{1+x} or $Fe_{1-x}S$
   2. Pentlandite $(Fe, Ni)_9S_8$–(Fe, Ni)S
   3. NiS and possibly others.

III. The Character of the Ore-forming Fluid from Which Common Iron and Nickel (and copper) Sulphides Are Deposited.

According to prevailing theories the ore-forming fluids may have been essentially dry sulphide melts, or hydrothermal solutions. The possibility that the ore-forming fluid may have varied in character from time to time and from place to place has also been considered. Such a compromise recognizes the lack of hydrothermal alteration associated with some ores and its presence in others.

In the present investigation the synthesis of iron and nickel sulphides has necessarily been confined to water-free melts and it is recognized that results and conclusions derived therefrom may not apply to such deposits formed solely by hydrothermal agencies.

Problems studied from this point of view, *i.e.*, a magmatic origin, consist of:

1. The question of the miscibility or partial miscibility of liquid iron and nickel sulphides.

2. The cooling history of iron and nickel sulphides and particularly the true relations of "ex-solution" pentlandite to pyrrhotite and of pyrrhotite to pentlandite.

3. The factors controlling the order of deposition of iron and nickel sulphides and apparent reversals in this order.

It should be clearly understood that no attempt is made here to deal with the larger problem of the character of the ore-forming fluids themselves. As detailed elsewhere [3] some experiments made in conjunction with this investigation emphasize the mobility of both iron and copper in the presence of H_2S. In sulphide deposits with no indication of contemporaneous hydrothermal activity there is little point in considering the volatility of metal chlorides or other evanescent halides on the one hand, or the solvent power of alkaline solutions on the other, and ignoring the possible importance of the really abundant volatile sulphur. The greatly increased carrying power of pure water at high, compared with low, temperatures and pressures suggests that the ability of H_2S to carry metals at high temperatures and under differential pressures should be investigated.

CRITICAL REVIEW OF THE LITERATURE.

1. On the Composition of Pyrrhotite and Pentlandite.

Pyrrhotite. Variation in sulphur of the pyrrhotite series of which troilite (FeS) is considered an end member has been shown by Allen, Crenshaw, Johnson, and Larsen [4] to be as much as 6.5 per cent, the equivalent formula being $Fe_1S_{1.18}$.[5]

Hägg and Sucksdorff [6] indicate that the excess sulphur may be due to the occurrence of vacant spaces in the iron lattice, rather than the introduction of extra S atoms. Recent work by Jensen [7] shows that if this explanation holds at high temperatures, the lattice has a maximum stability when there are a certain number of vacant iron positions, corresponding to a composition of $FeS_{1.08}$ or $Fe_{12}S_{13}$.

[3] Hawley, J. E.: Some heat effects on sulphides, Univ. Toronto Studies, No. 46: 33–38, 1941.

[4] Allen, E. T., Crenshaw, J. L., Johnson, J., and Larsen, E. S.: The mineral sulphides of iron. Am. Jour. Sci., 33: 200.

[5] Geophys. Lab., Annual Report. Pap., 595, p. 63.

[6] Hägg, Gunnar, and Sucksdorff, Ingrid: Die Kristallstruktur von Troilit and Magnetkies. Zeits. Phys. Chem., B, 22: 444–452, 1933.

[7] Jensen, E.: Pyrrhotite; melting relations and composition. Am. Jour. Sci., 240: 695–709, 1942.

According to Jensen the solubility of iron in FeS is negligible, though there is a possibility it may be greater at high temperatures. A review of the literature [8] by Jensen, to whose bibliography the reader is referred, shows that the limit of solubility of S in FeS at low temperatures is about 39.1 per cent S (as compared with 36.5 per cent S in FeS). This limit increases with increase in temperature to about 40.1 to 40.7 per cent at 677° C. The experimental data were limited, however, to below 693° C. at one atmosphere of S pressure, equal to the dissociation pressure of pyrite at this temperature.

Non-homogeneity of pyrrhotites from Norway has been described by Van der Veen,[9] and by Ramdohr and Schneiderhöhn,[10] and of specimens from Insizwa by Scholtz.[11] This shows by prolonged polishing or etching with HI. One of the two phases observed is darker and harder, the other paler and softer. Ramdohr suggests the undulating segregations or lamellæ are due to segregations of FeS from a sulphur-rich iron sulphide. Scholtz, for convenience, named the major, darker component, α—and the segration lamellæ, β—pyrrhotite. A quantitative association of secondary pentlandite with the β—phase of pyrrhotite led him to the belief that a nickel-rich solid solution had first separated from an original one, later ex-solving pentlandite, and the remaining β—pyrrhotite possibly still contained some nickel in solid solution.

The nickel content of pyrrhotite has been a debatable point since the discovery of the nickeliferous ores of Sudbury. Barlow's [12] first description in 1891 of nickeliferous "pyrrhotite" suggested Ni replaced Fe in the crystal structure. The recognition of

[8] Especially, Merwin, H. E., and Lombard, R. H.: The system Cu-Fe-S. Econ. Geol., XXXII: 203–284, 1937.

Roberts, H. S.: Jour. Am. Chem. Soc., 57: 1034–1038, 1935.

Juza, R., and Blitz, W.: Zeit. Anorg. Allgem. Chem., 205: 273–286, 1932.

Haraldsen, H.: Zeit. Anorg. Allgem. Chem. 231: 78–96, 1937.

[9] van der Veen, R. W.: Mineragraphy and Ore Deposition, Vol. I. 1925.

[10] Schneiderhöhn, H., and Ramdohr, R.: Lehrbuch der Erzmikroskopie. Berlin, 1931, 1934.

[11] Scholtz, D. L.: The magmatic Nickeliferous Ore Deposits of East Griqualand and Pondoland. Univ. Pretoria, 1936.

[12] Barlow, A. E.: Nickel and copper deposits of Sudbury. Can. Report, Geol. Surv., 1891, pp. 112–139.

polydymite in 1889 and of pentlandite in 1893 and studies by Bell[13] 1891, Emmens[14] 1892, Walker[15] 1894, and Dickson[16] in 1904, led to discussions pro and con the occurrence of specific nickel-bearing minerals within the pyrrhotite. With the advent of the polished section Dickson's conclusion that practically all nickel in pyrrhotite is accounted for by included particles of pentlandite was considerably substantiated by Schneiderhöhn and Ramdohr, and van der Veen and Ehrenberg. The latter showed the crystallographic orientation of blades of pentlandite in pyrrhotite to be such that the (111) and (110) planes of the former correspond with (0001) and ($10\bar{1}0$) planes respectively of pyrrhotite. Newhouse,[17] on the basis of his experimental results, suggested such secondary pentlandite could result on slow cooling from the breakdown of a pyrrhotite solid solution and believed that slow natural cooling would allow all the nickel to separate as pentlandite from pyrrhotite. By quick cooling, pyrrhotite with 13 per cent nickel remained a true solid solution.

Analyses of 21 pyrrhotites listed in Dana's System of mineralogy and some 36 given by Dickson show nickel varying from nil to 5.59 per cent, but none was subjected to microscopic examination. In general most of the nickel in pyrrhotite may be accounted for by blades or rims of pentlandite but it is neither certain that all the nickel would so separate nor that the cooling of ores in nature would always be such as to favor this separation. As indicated below primary pentlandite (*i.e.*, crystallized directly from a liquid) has also been noted in some ores.

[13] Bell, R.: The nickel and copper deposits of Sudbury district. G. S. A. Bull., 2: 125–140, 1891.

[14] Emmens, S. H., The constitution of nickeliferous pyrrhotite. Ont. Bur. Mines, 2nd Rept.: 163–166, 1892.

[15] Walker, T. L.: Notes on nickeliferous pyrite from Murray Mine, Sudbury, Ontario. Am. Jour. Sci., 47: 312–314, 1894.

Certain mineral occurrences in Worthington Mine, Sudbury, Ontario. Econ. Geol., 10: 539, 1915.

[16] Dickson, C. W.: The ore deposits of Sudbury, Ontario. A. I. M. E. Trans., XXXIV: 3–67.

[17] Newhouse, W. H.: The equilibrium diagram of pyrrhotite and pentlandite and their relations in natural occurrences. Econ. Geol., XXII: 288–299, 1927.

Pentlandite. The usual composition assigned to pentlandite is the original one proposed by Penfield,[18] as (Fe, Ni)S. Dickson [19] has shown that the ratio of (Fe + Ni) to S in many Sudbury pentlandite specimens is more correctly expressed as 11 : 10 than as 1 : 1, and that the simpler ratio given by Penfield was due to an error in calculation. Fe : Ni in the Sudbury specimens is also quite constant, 10 : 11, and the ratio of nickel to cobalt is about 42 : 1. In contrast, pentlandite from Lillehammer,[20] Norway has 19 to 22 per cent nickel and corresponds more with the formula (2FeS.NiS).

Analyses of pentlandite are given in Table I.

TABLE I.

ANALYSES OF PENTLANDITE.

	S	Fe	Ni	Cu	Co	Total	
1. Lillehammer	36.45	42.70	18.35	1.16		98.66	Dana System
2. Lillehammer	36.64	40.21	21.07	1.78			Dana System
3. Lillehammer (Recal. No. 1)	37.40	43.5	19.1			100.00	
4. Sudbury	34.25	25.81	39.85	0.24			Dana System
5. Sudbury Frood	33.30	30.04	34.98		0.85	99.17	Dickson
6. Sudbury Creighton	32.90	30.00	34.82		0.84	98.56	Dickson
7. Sudbury Copper Cliff	33.42	30.25	34.23		0.85	98.75	Dickson
8. Sudbury Av. 5–6–7	33.72	30.55	35.73			100.00	Dickson
9. Sudbury	37.00	29.1	33.90			100.00	Zurbrigg-S by diff.
Theoretical.							
10. 45FeS/55NiS	35.92	28.51	35.57			100.00	(by weight)
11. FeS.NiS	35.9	31.2	32.9			100.00	(Mol. ratio)
12. $(FeS)_2.Ni_2S_2$	29.6	19.1	51.3			100.00	(Vogel-Tonn)
13. $(Ni.Fe)_9S_8$	32.8	31.85	35.35			100.00	Ni:Fe = 11:10

Newhouse [21] determined the melting point of Sudbury pentlandite as about 878° C., and noted that the temperature range suggests it is a solid solution. Pentlandite with prolonged heat-

[18] Penfield, S. L.: On pentlandite from Sudbury, Ontario. Am. Jour. Sci., 45: 492–497,1893.

[19] Dickson, C. W.: op. cit., pp. 21–23.

[20] Dana, J. D.: System of Mineralogy, 6th edit. John Wiley, New York, 1892. P. 65.

[21] Newhouse, W. H.: op. cit., p. 290.

ing above its melting point breaks up into two components, FeS + xS and a white substance possibly Ni_3S_2 This breakdown, particularly if accompanied by loss of sulphur (as will be seen later), might be considered a case of incongruent melting with formation of a nickel-rich liquid and pyrrhotite crystals, the liquid portion crystallizing to a nickel sulphide on quenching. Or, loss of sulphur during the melting of pentlandite, may so change the composition that an Fe-Ni alloy will form along with a pyrrhotite.

Gruner [22] apparently from x-ray data of Alsen [23] suggests that the atomic structure is that of a sulpho-salt with a formula $(Ni, Fe)_3FeS_4$; the iron atoms replaceable by Ni do not have equivalent positions in the structure to other iron atoms. If this is the case the maximum nickel in a unit cube would be 24Ni to 8Fe and 32S or (Ni_3FeS_4).

Lindqvist, Lundqvist and Westgren (1936) [24] studied Sudbury pentlanite and Co_9S_8 and concluded from the similarity of their structures that the formula of pentlandite is best represented by $(Ni, Fe)_9S_8$. They showed that in Alsen's structure sulphur atoms were located on the points where there are metal atoms and vice versa.

These authors also prepared two artificial pentlandite specimens corresponding to $Fe_9Ni_9S_{16}$ and $Fe_6Ni_3S_8$, but in powder photographs found, besides the cubic sulphide, faint lines of pyrrhotite, so the *artifical pentlandite* in each case must have been richer in nickel than is indicated *by the proportions of the original mixtures,* and the limits of substitution of Ni for Fe are thus still undefined.

Analytical work on pentlandite has been confined largely to coarse-grained specimens or concentrates made magnetically from pyrrhotite and analyses of the latter type no doubt represent an

[22] Gruner, J. W.: Structures of sulphides and sulpho-salts. Am. Min., 14: 480–481, 1929.

[23] Alsen, N.: Geol. Förhandl, 1925, pp. 47, 54.

[24] Lindqvist, M., Lundqvist, D., and Westgren, A.: The crystal structure of Co_9S_8 and pentlandite $(Ni.Fe)_9S_8$. Svensk Kemisk Tidskrift, 1936, pp. 156–160.

average. No specific data are available to show if the pentlandite occurring in both fine and coarse intergrowths is the same in composition or varies. According to Dickson [25] the composition of the Sudbury mineral, obtained from various separate deposits, is surprisingly constant.

Hewitt [26] has shown however that on slow cooling of nickeliferous pyrrhotite, pentlandite unmixed from a solid solution. This gave rise to symmetrically oriented laths of a substance similar to, if not identical with, pyrrhotite and visible at magnifications over 1,000. This suggests that the original solid solution broke down to a pyrrhotite and an iron-rich pentlandite solid solution which in turn exsolved excess FeS or pyrrhotite, but whether or not equilibrium had been attained on the first unmixing of pentlandite is not clear. There is some question whether the second generation of pyrrhotite blades represent either remnants of original pyrrhotite unreplaced by pentlandite, or an actual ex-solution product. It should be noted that in other experiments, prolonged heating at high temperature causes a loss of sulphur, and even in sealed tubes, as used by Hewitt, the sublimation of crystals of pyrrhotite above a specimen of intergrown pyrrhotite and pentlandite would result in the partial desulphurization of the natural minerals remaining in the base of the tube. The influence of such a loss of sulphur has still to be considered.

An iron-rich type of natural pentlandite from Lillehammer has been noted, but Sudbury specimens are fairly constant in composition and richer in nickel. Whether or not fine and coarse intergrowths of the mineral with pyrrhotite have the same composition is undetermined. Artificial pentlandites may be made which show a variation in the Fe : Ni ratio but the stability of these and their range in composition at both elevated and low temperatures is not certain. Neither is there information on the possible variations in sulphur content of this mineral.

[25] Dickson, C. W.: op. cit., p. 21.

[26] Hewitt, R. L.: Experiments bearing on the relation of pyrrhotite to other sulphides. Econ. Geol., XXXIII: 305–338, 1938.

2. Crystal Phases of Minerals in the Fe-Ni-S System.

The problem of the possible crystal phases of pentlandite, pyrrhotite, and NiS at elevated temperatures naturally arises, since the subject of solid solution of (cubic) pentlandite and (hexagonal) pyrrhotite is involved in this system.

Pyrrhotite has long been listed in Dana as existing in two crystal modifications, hexagonal at ordinary temperatures and orthorhombic above 138° C. X-ray studies reported in the Annual Report of the Director of Geophysical Laboratory [27] for 1939–40 indicate that three different phases may be distinguished in the sulphur-rich series of solid solutions between room temperature and 350° C.[28]

Most x-ray studies of *pentlandite* have apparently been limited to the cubic form stable at low temperatures. Alsen [29] reports that after calcination pentlandite becomes trigonal.

The monosulphide of nickel has two crystalline forms, the hexagonal NiAs type, usually exhibited by synthetic NiS, and the rhombohedral, millerite type, always exhibited by the natural mineral. NiS_2 is cubic and of the pyrite type.

Thermal studies of the compound $2FeS.Ni_3S_2$ in the system $FeS–Ni_3S_2$ by Vogel and Tonn [30] indicated a polymorphic transformation of the compound at 615° C. The solubility of Fe and Ni metals in the compound appears related to this transformation. Similar thermal data suggest that a ternary solid solution (corresponding to pentlandite as shown later) undergoes a crystal change at about 575° C.

[27] Pub. 1030, 1939–1940.

[28] Jensen (op. cit., p. 706) calls attention to the transformations of pyrrhotite indicated by Roberts and cthers and notes there is no evidence for a transformation above 800° C. Though not included on Jensen's diagram, a transformation has been suggested between 550° C. and 575° C. A sharp, reversible one occurs at 315°–318° C. which is constant even with variable sulphur. Still a third occurs between 144° and 139° to give the stable low temperature form. The temperature of the latter inversion decreases with increasing sulphur. Still other phases may be present in high-sulphur pyrrhotites but data as to their crystallography are not available.

[29] Alsen, N.: Geol. for Stock. Fröh., 1925, pp. 47, 191.

[30] Vogel and Tonn: The Ternary System Fe-Ni-S. Arch. f. d., Eisenhuttenwesen, 12: 769, 1930.

3. On the Relations of Pyrrhotite and Pentlandite in Ores.

Studies of the literature and of polished sections of ores from different deposits containing pyrrhotite, pentlandite, and usually chalcopyrite leave the question of the age relations of these minerals in a somewhat confused state. It is now recognized that much of the pentlandite, particularly that showing bladed, dendritic, or flame-like, and cell or net types of textures with respect to pyrrhotite, is the result of the breakdown of solid solutions, and there is a tendency to the conclusion that all pentlandite is of this origin.

Early investigators such as Campbell and Knight,[31] and later Wandke and Hoffman,[32] Lindgren and Davy,[33] Tolman and Rogers,[34] place the general sequence of deposition as pyrrhotite-pentlandite-chalcopyrite. Kerr [35] notes two generations of pentlandite, a first, following pyrrhotite, and a second due to exsolution phenomena. Agar [36] found both pentlandite and chalcopyrite invading and cutting through pyrrhotite, but since pyrrhotite shows no fracturing and cross-cutting relations between pentlandite and chalcopyrite are not apparent, the three sulphides are considered contemporaneous.

Goodchild [37] notes that the common order of deposition of copper-nickel-iron sulphides in the Insizwa deposits is the reverse of that at Sudbury, namely, (1) chalcopyrite, (2) pentlandite, and (3) pyrrhotite. He argues for a magmatic rather than hydrothermal origin, and suggests "differential liquation" as a process affording an adequate explanation of the mineral relationships.

[31] Campbell, W., and Knight, C. W.: Microscopic examination of nickeliferous pyrrhotites. Eng. and Min. Jour., Nov. 17, 1906; ECON. GEOL., II: 350–366, 1907.

[32] Wandke, A., and Hoffman, R.: A study of the Sudbury ore deposits. ECON. GEOL., XIX: pp. 169–204, 1924.

[33] Lindgren, W., and Davy, W. M.: Nickel ores from Key West Mine, Nevada. ECON. GEOL., XIX: 309–319, 1924.

[34] Tolman, C. F., and Rogers, A. F.: A study of magmatic sulphide ores. Stanford Univ., Pub. Ser., 76: 31–37, 1916.

[35] Kerr, P. F., A magmatic sulphide ore from Alaska. ECON. GEOL., XIX: 369–376, 1924.

[36] Agar, W. M.: The Hodges nickel prospect, Connecticut. Am. Jour. Sci., 5th Ser., 19: 185–194, 1930.

[37] Goodchild, W. H.: ECON. GEOL., XI: 397–402, 1916.

Phemister [38] corroborates Goodchild's conclusion for the order of deposition of the sulphides in disseminated ore, but notes that pentlandite was the first mineral to form in massive sulphides, followed by pyrrhotite, and, presumably by chalcopyrite. He favors a hydrothermal origin for the ores, based largely on the occurrence of early quartz within the sulphides.

As noted by Scholtz,[39] who made a much more complete study of the Insizwa deposits than either Goodchild or Phemister, the general order of deposition of the simple sulphides is pyrrhotite, pentlandite, and chalcopyrite. The pentlandite is of two generations. Details of his paragenesis and origin for this ore are given below in chronologic order, since some of his conclusions have been influenced by earlier work of other investigators.

In the British Columbia Nickel Mines, Yale District, in which the host rock is hornblendite, Cockfield and Walker [40] consider pentlandite formed before pyrrhotite and chalcopyrite, which appear contemporaneous since they vein each other. Horwood [41] in a later study notes that most of the pentlandite crystallized before the pyrrhotite, but some of it is undoubtedly later. Early pentlandite is corroded and replaced along cleavages by pyrrhotite. He suggests the period of pentlandite crystallization began before and continued until after that of pyrrhotite. No mention is made of the separation of pentlandite from pyrrhotite, though "needles of pentlandite projecting out into pyrrhotite from a narrow crack" might be so interpreted.

As stated by Hewitt,[42] Schneiderhöhn and van der Veen [43] favor the idea that pentlandite and pyrrhotite unmix at high temperature with, in general, the complete separation of the two.

[38] Phemister, T. C., A microscopic examination of the Insizwa sulphide deposits. Inst. Min. Met. Trans., XXXIII: 519–524, 1924.

[39] Scholtz, D. L.: op. cit., pp. 156–169.

[40] Cockfield, W. E., and Walker, J. F.: The nickel-bearing rocks near Choate, British Columbia. Canada Geol. Surv. Summ. Rept., 1933, Pt. A, p. 66.

[41] Horwood, H. C.: Geology and mineral deposits of the mine of British Columbia Nickel Mines, Ltd., Yale District, B. C. Canada Geol. Surv. Mem., 190: 11, 1936.

[42] Hewitt: op. cit., p. 308.

[43] Schneiderhöhn, H., and van der Veen, R. W.: op. cit.

Newhouse [44] on a basis of microscopic studies and experiments concludes that the relations between the two minerals may be explained in part by the breakdown of a solid solution and in part by the segregation of liquid pentlandite which would crystallize after the pyrrhotite. This is the first suggestion in American literature that the iron and nickel sulphides form immiscible or partially miscible liquids, though Goodchild's suggestion of "differential liquation" as noted above, was made some years previously.

The conclusions of Scholtz [45] regarding the paragenesis of pyrrhotite and pentlandite are worth citing, since they differ from others made on the Insizwa ores.

1. The fact that pentlandite is present in the genetically related pyrrhotite-bearing and pyrrhotite-free varieties of ore shows that the former was still separating after crystallization of the pyrrhotite. That the copper-enriched residues remaining after the separation of all the pyrrhotite still contained much nickel is indicated by the abundance of pentlandite in the sheets of chalcopyrite-cubanite ore.

2. The marginal and intergranular distribution of the largest aggregates of pentlandite with reference to pyrrhotite, as well as the characteristic pentlandite fringes about intrusive veins of chalcopyrite, suggests that much of the pentlandite—crystallized after the pyrrhotite and before the chalcopyrite.

3. That the narrow vein-like masses of pentlandite inclined or parallel to the (0001) parting in pyrrhotite cannot be regarded as providing adequate evidence of the invasion of the latter by the former, since much, if not all, of its substances may be secondary (*i.e.*, ex-solution) origin.

4. Secondary pentlandite contributed to the substance of the massive primary pentlandite, by merging insensibly with the latter. Marginal inclusions of pyrrhotite are, therefore, regarded as remnants and not as advance islands which replace pentlandite. Secondary pentlandite may assume definite crystalline boundaries in pyrrhotite.

5. The fact that veinlets of pyrrhotite appear to penetrate the margins of aggregates of primary pentlandite along directions approximately parallel to the trace of its octahedral cleavage cannot be considered as a criterion of the later crystallization of the former, since the more massive clusters of pentlandite often grade marginally into secondary pentlandite which has been shown to be definitely oriented in the pyrrhotite.

[44] Newhouse, W. H.: op. cit., p. 298.

[45] Scholtz, D. L.: op. cit., pp. 160–161.

The above summary thus serves to correct previous interpretations for this ore, and leaves the British Columbia nickel deposit as the only one illustrating the early crystallization of pentlandite prior to that of pyrrhotite.

Accepting Newhouse's suggestion of partial miscibility of pyrrhotite and pentlandite liquids, Scholtz considers that a major portion of the pentlandite separated in the liquid state from pyrrhotite which itself, on first crystallizing, held some Ni in solid solution; that pentlandite continued to crystallize after the pyrrhotite; and that ex-solution pentlandite contributed to the substance of massive primary pentlandite by merging insensibly with it. He also notes the close association of "flames" of exsolution pentlandite within a (β—) segregated phase of pyrrhotite as noted above.

Schwartz [46] in his detailed review of the occurrence of pyrrhotite notes that, in general, pentlandite is contemporaneous with pyrrhotite but "commonly shows a continuation of deposition beyond the latter."

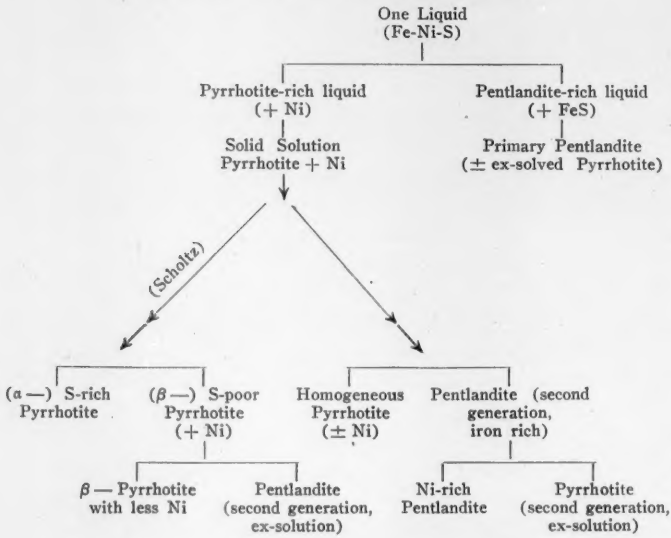
Hewitt [47] from studies of the behavior of pyrrhotite and pentlandite under heat established that pentlandite goes into solution in pyrrhotite between 425° and 450° C., and may separate on slow cooling from above 800° C. Slow cooling from temperatures between 450° and 800° C., however, did not bring about any such separation. The occurrence of unmixed laths of pyrrhotite (?) within ex-solved pentlandite is attributed either to the partial miscibility, rather than complete immiscibility, of the two liquid substances, or to the breakdown of pentlandite, expelling pyrrhotite. He, too, is of the opinion "that large masses of pentlandite are produced by crystallization from a field of immiscible liquids," and "small pentlandite grains occurring around pyrrhotite boundaries or as lenses within pyrrhotite grains occurring around pyrrhotite boundaries or as lenses within pyrrhotite are the product of unmixing."

[46] Schwartz, G. M.: The paragenesis of pyrrhotite. ECON. GEOL., XXXII: 53, 1937.

[47] Hewitt, R. L.: op. cit., pp. 317–318.

The history of the crystallization of an iron-nickel and sulphur liquid such as would form a pyrrhotite-pentlandite ore, from the work of Newhouse, Scholtz and Hewitt may be summarized in tabular form thus:

SUGGESTED CRYSTALLIZATION OF AN Fe-Ni-S LIQUID



4. Experimental Investigations of Fe-Ni-S System.

Little has been published in English on this system, aside from results of studies of the binary systems which form the boundaries for the ternary diagram Fe-S, Fe-Ni, and Ni-S. The more important contributions are metallurgical in character, recently summarized in an article by Urazov and Filin [48] in Russian.[49] To these may be added the investigations by Newhouse and Hewitt on pyrrhotite and pentlandite. Metallurgical studies approach the

[48] Urazov, G. G., and Filin, N. A.: Investigations of iron-nickel-sulphur system. Metallurg., 13: 3–17, 1938 (in Russian).

[49] The writers are indebted to Professor G. Krotkov, Queen's University for a translation of the paper by Urazov and Filin.

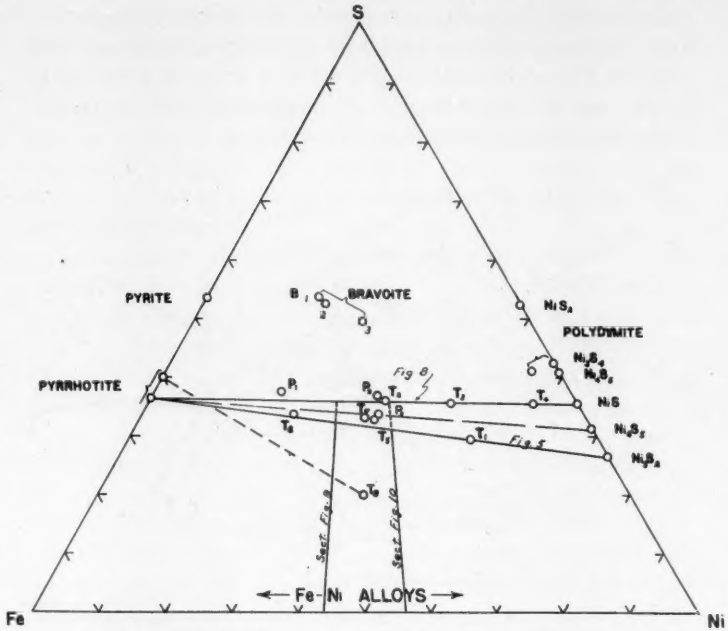


FIG. 1. Composition diagram of the ternary Fe-Ni-S System showing composition of minerals occurring in the system, synthetic pentlandites, and other compounds. Lines are drawn along some of the sections which have been investigated experimentally.

P_1—Lillehammer pentlandite.
P_2—Pentlandite—analysis No. 9, Table 1.
P_3—Pentlandite—analysis No. 8, Table 1.
T_1—Ternary compound $(FeS)_2Ni_3S_2$.
T_2—Synthetic pentlandite from melt of 55NiS-45FeS.
T_3—Synthetic pentlandite from melt of composition 70NiS-30FeS.
T_4—Synthetic pentlandite from melt of 90NiS-10FeS.
T_5—$(Ni, Fe)_9S_8$ with Ni : Fe = 11 : 10 calculated.
T_6—$Fe_4Ni_5S_8$ (synthetic pentlandite) of Lindqvist et al.
T_7—$Fe_9Ni_9S_{16}$ (synthetic pentlandite) of Lindqvist et al.
T_8—Fe40, Ni40, S20, mix of Newhouse.
Pd—Polydymite—Dana's System.
B_1—Bravoite—(Bannister).
B_2—Bravoite—Tasmania (Bannister).
B_3—Bravoite—Peru (Bannister).

region in the ternary diagram in which the natural minerals pyrrhotite and pentlandite are found and show fields of solid solutions of Ni in FeS and a ternary solid solution series to which pentlandite may belong (Fig. 1). It is pertinent then to review briefly the available information of this type.

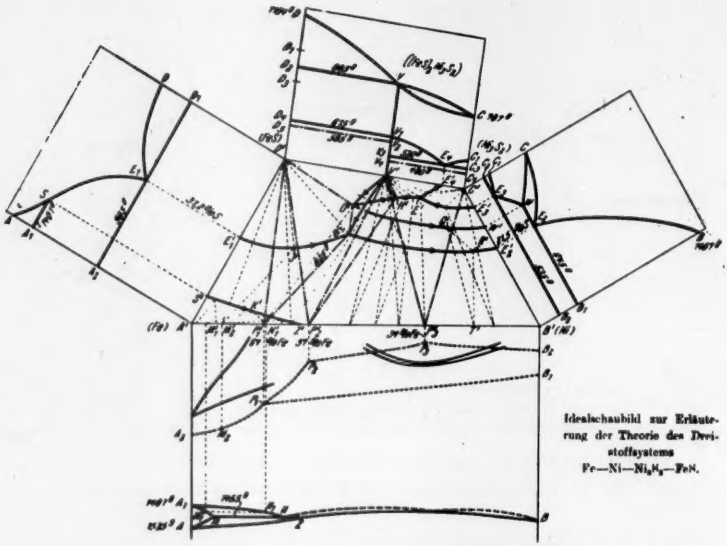


FIG. 2. Photograph of an illustration given by Vogel and Tonn in their paper on the System Fe-Ni-Ni_3S_2 in Arch. f. d. Eisenhuttenwessen, 12: 769, 1930. Acknowledgment is made as permission for this reproduction cannot be obtained during the war. Attention is called to the diagrams on the boundary surfaces of this system. Partial explanations are given under different headings below.

The System Fe-Ni. Fe and Ni form a series of solid solutions on crystallizing and these, in the region between 9 and 32 per cent Ni, and again between 32 and 100 per cent Ni, undergo transformation on cooling. References on this system include articles

by Osmond,[50] Benedicks,[51] Guertler and Tommann,[52] Osmond,[53] Ruer and Schulz,[54] Hanson,[55] and Hanson and Freeman [56] (Fig. 2).

The System Fe-S has been much investigated but our knowledge, as shown by the recent work of Jensen,[57] is still incomplete. Figure 3 is a diagram based largely on data given by Jensen on the stability field of pyrrhotite and in part is after Vogel and Tonn and Urazov and Filin.

Crystallization of melts between Fe and FeS yields γ-Fe with a minor amount of S in solid solution, and FeS which crystallize at a eutectic at about 980° C. at a composition of 68.5 to 69 per cent Fe. From the eutectic to a composition of 61.7 per cent Fe (52 atomic per cent S) the crystallization temperature of pyrrhotite rises to a maximum (1191° C.) where the composition $Fe_{12}S_{13}$ forms, like a simple compound. Jensen indicates that the composition "FeS melts over a large temperature interval with dissociation into a solid richer in sulphur and a liquid richer in iron." With still higher sulphur (to over 40 per cent by weight) crystallization of pyrrhotite proceeds at lower temperatures and over an interval "like a solid solution." Beyond this concentration of S, Jensen notes that "the only thing known about the temperature of the supposed eutectic between pyrite and pyrrhotite is that it must be between 693° and 1,091° C.

Transformations of pyrrhotite have been noted on page 354.

The System Ni-S. Bornemann,[58] Vogel and Tonn,[59] and Guertler and Savelsberg [60] present results on that part of the sys-

[50] Osmond: Comptes Rendus, 126: 308, 1899.
[51] Benedicks: Kolloid Zeitschrift, 7: 290, 1900.
[52] Guertler and Tommann: Z. Anorg. Chem., 45: 211, 1905.
[53] Osmond: Revue de Metallurgie, 2: 748, 1907.
[54] Ruer and Schulz: Metallurgie, 7: 415, 1910.
[55] Hanson: Jour. Iron and Steel Inst., London, 102: 39, 1920.
[56] Hanson and Freeman: Jour. Iron and Steel Inst., London, 107: 301, 1923.
[57] Jensen, E.: op. cit., pp. 695–709.
[58] Bornemann: Metallurgie, 5, 1908; 7, 1910.
[59] Vogel and Tonn: op. cit.
[60] Guertler and Savelsberg: The ternary system Fe-Ni-S. Metal. u. Erz., 5: 84–91, 1932.

tem Ni-S from Ni to Ni_3S_2 and to Ni_6S_5 respectively. Urazov and Filin give a diagram modified after Bornemann (Fig. 4). The

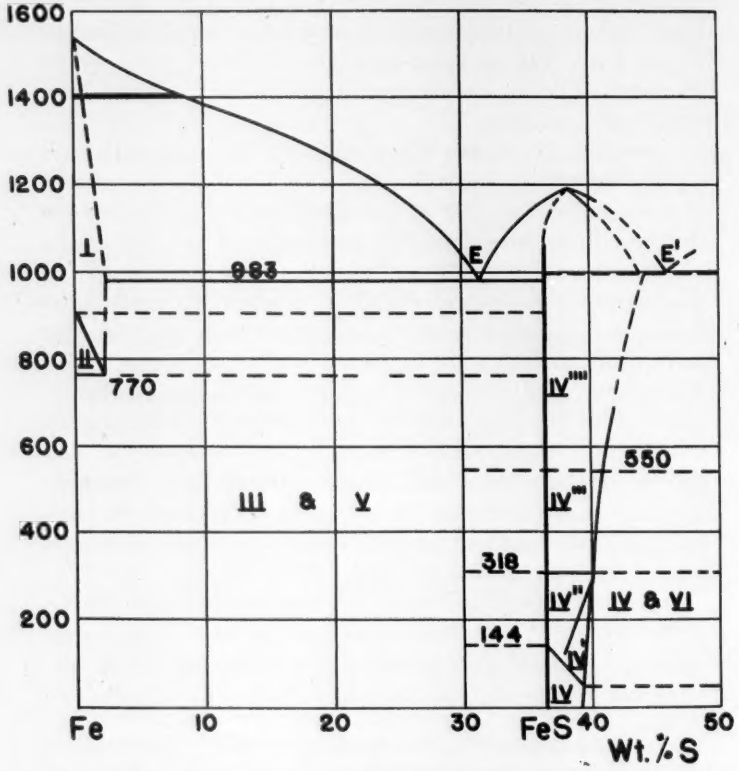


FIG. 3. Fe-S System after Jensen, Vogel and Tonn, and Urazov and Filin. Fields indicated are I-γ-Fe, IIβ-Fe, IIIα-Fe, IV-pyrrhotite, V-FeS, VI-pyrite.

melting point of Ni, 1,452° C., is lowered by addition of sulphur till a eutectic is reached at 645° C. at a composition of 23 per cent sulphur. At this point β-nickel and Ni-S solid solution crystal-

laize. β-nickel is considered to dissolve sulphur up to 4 per cent at 1,300° C. but this decreases to zero at 535° C. Ni_3S_2, crystallizing at 787° C., may be considered to form a solid solution with Ni and vary in composition from 26.8 per cent to 24 per cent

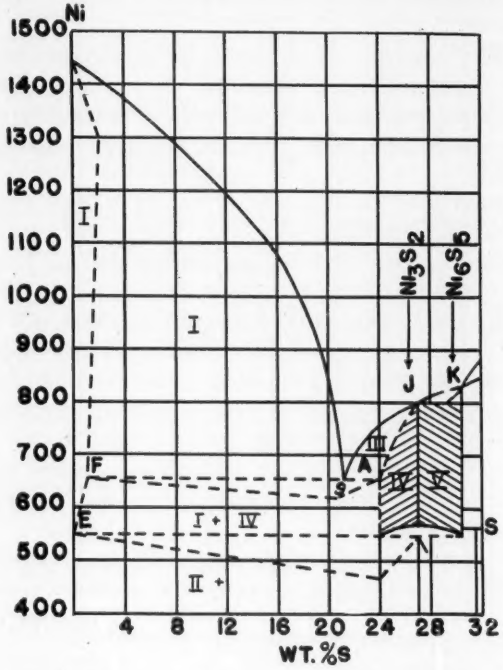


FIG. 4. Ni-S System after Urazov and Filin. Fields—I-β-nickel, II-α-nickel, III-Ni_3S_2 solid solution plus liquid, IV-Ni_3S_2 solid solution, V-Ni_6S_5-solid solution.

sulphur. On cooling below 535° C., Guertler records that Ni_3S_2 breaks down to Ni_6S_5 and Ni, but other investigators have not found this to be the case. With higher concentrations of sulphur (above Ni_3S_2) solid solution of Ni and S form, which on cooling, gives rise to Ni_6S_5 which is stable down to room temperatures.

Schenk and Forst[61] investigated the Ni-Sb-S System and studied the reaction of H_2S on NiS. At 600° C. and 29.8 per cent H_2S the two phases in equilibrium are NiS and γ-solid solution. At 400° C. and 13.6 per cent H_2S, NiS and Ni_6S_5 exist in equilibrium but with 4.6 per cent H_2S, Ni_6S_5 and Ni_3S_2 are in equilibrium.

FeS-Ni_3S_2 System. Investigation of this system by Bornemann,[62] Vogel and Tonn,[63] Guertler,[64] and Urazov and Filin[65] show it to be a true binary at high temperatures but different interpretations have been made from thermal and microscopic data obtained.

Vogel and Tonn show in section *D'C'* (FeS-Ni_3S_2) of Fig. 2 the formation of a compound $(FeS)_2.Ni_3S_2$ noted previously by Bornemann. Above 885° C. and between FeS and the compound, crystals of FeS form at decreasing temperatures with increase of Ni_3S_2. Between the compound and Ni_3S_2 (M.P. 787° C.) is a continuous series of solid solutions which subsequently break down according to a eutectoid reaction with the formation of the compound and Ni_3S_2. The compound, crystallizing at 885° C., undergoes a polymorphic transformation at 615° C.

Guertler's studies indicate that neither the compound nor Ni_3S_2 are stable down to room temperatures but break up into FeS, Ni_6S_5 and Ni $\pm$ a little Fe.

Bornemann, according to Urazov and Filin, noted also that FeS takes up Ni to yield solid solutions up to a maximum, corresponding to 2.5 per cent Ni_3S_2 or 1.83 per cent Ni. This decreases on cooling to 1 per cent Ni_3S_2 at 500° C.

Urazov and Filin on the other hand indicate that melts between FeS and $(FeS)_2.Ni_3S_2$ yield solid solution crystals of FeS + Ni varying in composition along the line *AE* (Fig. 5) and that between composition *E* to *B* a peritectic reaction occurs between these and a final liquid of composition $(2FeS).Ni_3S_2$ or (42.5 per

[61] Schenk and Forst: The system Ni-S. Zeit. für Anorg. Chem., 1939.
[62] Bornemann: op. cit.
[63] Vogel and Tonn: op. cit.
[64] Guertler and Savelsberg: op. cit.
[65] Urazov and Filin: op. cit.

cent nickel) forming solid solution crystals of composition *D* (30 per cent nickel) at a temperature estimated at 870° C from

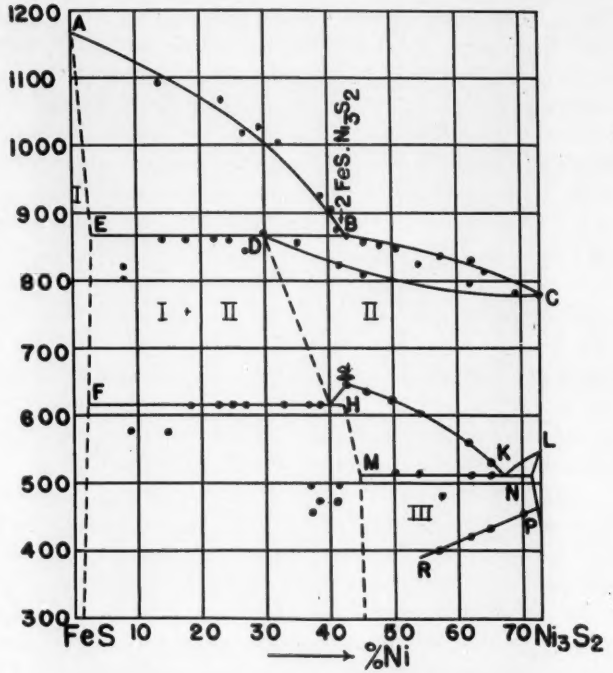


FIG. 5. FeS-Ni_3S_2 System after Urazov and Filin illustrating a peritectic reaction between FeS(+ Ni) crystals of composition E and liquid composition B to form ternary solid solution D. Fields—I-FeS solid solution with maximum of 1.83 per cent Ni, II-ternary solid solution, III-eutectoid of ternary compound $(FeS)_2Ni_3S_2$ and Ni_3S_2. Line F H marks a transformation of the ternary compound.

their diagram. Between $(FeS)_2.Ni_3S_2$ and Ni_3S_2 is a continuous series of solid solutions.

On cooling the solid solution *D* ex-solves FeS with a little Ni in solid solution and changes in composition, becoming more Ni-rich

until the transformation temperature H is reached. At H, at constant temperature, the remainder of the iron is ex-solved as iron sulphide and there exists a mixture of pure $2FeS.Ni_3S_2$ and $FeS + Ni$ in solid solution. Solid solution between C and the $2FeS.Ni_3S_2$ composition line, likewise breaks up into crystals of the compound Ni_3S_2 with the formation of a eutectoid at K, temperature of 515° C. Temperature breaks along line FH correspond to a transformation in the compound, which results in the liberation of some free metals according to the authors. Other breaks noted on the right (RP) are not interpreted. Those on the left of M between 450° C. and 500° C. are thought to represent a breakdown of the compound.

FeS-Ni_6S_5 System. Four of Guertler's and Savelsberg's melts of Fe, Ni and S fall on the "Quasi"-binary section FeS-Ni_6S_5. They record homogeneous solid solutions in both iron-rich and nickel-rich melts; with intermediate compositions they consider that an original solid solution formed which decomposed to a eutectoid of FeS and Ni_6S_5, but sufficient data were not obtained to establish a diagram for this section of the ternary system.

Fe-Ni-S System. Isothermal diagrams covering that part of the ternary system bounded by Fe, FeS, Ni_3S_2, Ni have been prepared by Vogel and Tonn and Urazov and Filin, as a result of experimental work on melts chosen along sections running from the Fe-Ni boundary toward the apex of the composition diagram representing 100 per cent sulphur. Vogel and Tonn also present their results in a photograph of a three-dimensional model (Fig. 6).

The liquidus surface is divided into three main areas of primary crystallization. The steeply sloping surface (Fig. 6) of A (Fe), B (Ni), E_2GE_1 corresponds to the crystallization of Fe-Ni solid solutions. A fourth surface of crystallization of Fe-Ni solid solutions is represented by AZS. (See also Fig. 2.)

The field $DVGE_1$ represents the crystallization of FeS which actually should contain some nickel in solid solution. From the field VGE_2C ternary solid solutions crystallize. VG is the boundary line between these fields, and lines E_1G and GE_2 repre-

sent the lines of eutectic crystallization between (Fe-Ni) solid solutions and FeS on the one hand and ternary solid solutions on the other. At *G* (*G'* of Fig. 2) a four phase reaction takes place at about 825° C., the phases being (Fe-Ni) mix crystals (64%

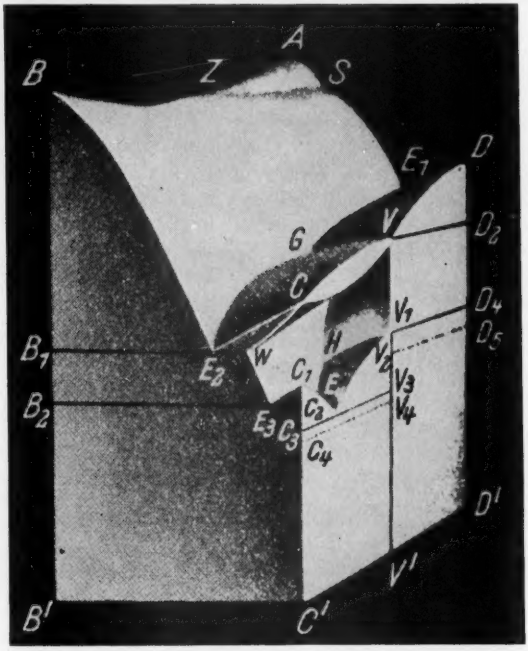


FIG. 6. Fe-Ni-FeS-Ni_3S_2 System. Photograph of a model after Vogel and Tonn published in Arch. f. d. Eisenhuttenwesen, 12, 1930, p. 769, acknowledgment of which is made as permission for this reproduction cannot be obtained during the war. *A*-Fe, *B*-Ni, *D*-FeS, *C*-N_3S_2.

Fe), FeS, and ternary mix crystals of composition *O'* (39% Fe-29% S) (Fig. 2) and liquid of composition *C'*. A second transition plane is fixed at about 585° C. with the decomposition of the ternary mix crystals, the resulting phases being Fe-Ni mix crys-

tals (P_2) (Fig. 2), FeS, ternary compound $(FeS)_2.Ni_3S_2$, and ternary mix crystal H' (26% Fe-28% S).

The region $O'W'C'V'$ (Fig. 2) represents the field of existence of ternary solid solutions (Fe-Ni-S) which decompose on cooling as does mix crystal E'_4 at about 480° C. with the formation of a ternary eutectic E' consisting of Fe-Ni of composition P_3 (34% Fe), ternary compound $(FeS)_2.Ni_3S_2$ and Ni_3S_2.

As noted above, the work of Guertler and Savelsberg [66] alone suggested the breakdown on further cooling of the ternary compound and Ni_3S_2 to form FeS, Ni_6S_5 and Ni (or Fe-Ni).

Modifications made by Urazov and Filin are shown in Fig. 7

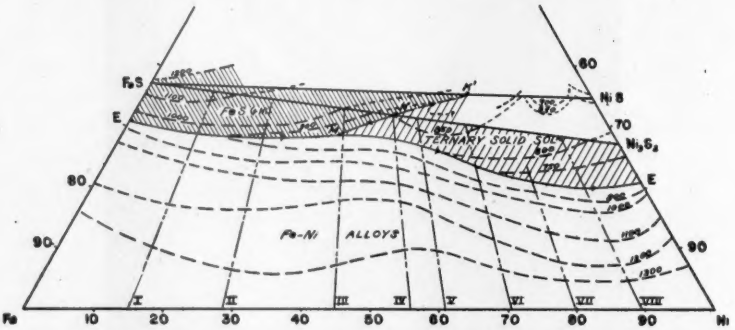


FIG. 7. Isothermal diagram of part of Fe-Ni-S System Urazov and Filin, to which new data are added, showing surfaces of primary crystallization. Sections I–VIII investigated by Urazov and Filin.

where the three crystallization surfaces are shown for solid solution of Fe-Ni, ternary solid solution, and FeS. The line KM between the fields of FeS and ternary solid solution marks the limits at which the peritectic reaction takes place between FeS-rich crystals and liquid. At M presumably the three phases listed are in equilibrium. The ternary solid solutions are not stable and break down as shown by Vogel and Tonn to $2FeS.Ni_3S_2$ and Ni_3S_2. The ternary eutectoid of the latter authors was not found.

[66] Guertler and Savelsberg: op. cit.

In summary we may note the following from all investigators:

1. Only one liquid phase was found though the possibility of immiscible liquids was considered by Vogel and Tonn.

2. Primary crystallization yields FeS, with some Ni in solid solution (though little attention is paid to it except on the FeS-Ni_3S_2 section), ternary solid solution Fe-Ni-S, and Fe-Ni alloys.

3. Along the FeS-Ni_3S_2 section a typical peritectic reaction is indicated by Urazov and Filin as taking place between FeS ($\pm$ Ni) crystals and liquid to form a ternary solid solution.

4. Ternary solid solutions in the high temperature region range in composition on the FeS-Ni_3S_2 section from 30 per cent Ni to 73.3 per cent Ni in Ni_3S_2.

5. In all cases the ternary solid solutions break down to the compounds $(FeS)_2.Ni_3S_2$ and Ni_3S_2. According to one author these further separate into FeS, Ni_6S_8 and Fe-Ni alloy, but this has not been corroborated by others and may be questioned.

6. In the metallurgical investigations FeS has been recognized as similar to troilite or pyrrhotite but none of the other products have been referred to natural minerals. Ni_3S_2 does not occur as such. The question arises then as to whether or not the ternary solid solution (Fe-Ni-S) and the compound $(FeS)_2.Ni_3S_2$ are related to the mineral pentlandite $(Fe, Ni)_9S_8$ and if so just what relationship exists. Unfortunately metallurgical descriptions of the ternary solid solutions in the FeS-Ni_3S_2 System do not indicate whether they are cubic or not. We may note, however, that the synthetic pentlandites, $Fe_6Ni_3S_8$ and $Fe_9Ni_9S_{16}$ of Lundqvist fall either on or close to the FeS-Ni_3S_2 section (Fig. 1) though the exact composition of these has been questioned above. Analyses of other pentlandites show they are somewhat richer in sulphur than the ternary solid solution series referred to. Natural pentlandite is a stable compound whereas the ternary solid solutions break up at low temperatures into the compound $(FeS)_2.Ni_3S_2$ and Ni_3S_2. If the two are related is this difference in stability attributable to sulphur content?

Experiments by Newhouse. By melting mixtures of iron, nickel and sulphur calculated into various percentages of FeS + 5 per cent excess S, and of (Fe.Ni)S, Newhouse[67] prepared a phase diagram showing equilibrium relations of pyrrhotite and pentlandite. Cooling curves and products suggested that pyrrhotite with nickel in solid solution crystallized first, that pent-

[67] Newhouse, W. H.: op. cit., p. 292.

landite liquid may have separated from the iron-rich liquid, and subsequently crystallized directly to form primary pentlandite at about 870° C. The natural mineral pentlandite was found to melt at 878° C. From the pyrrhotite solid solutions containing above 13 per cent nickel, secondary pentlandite was found to exsolve at an undetermined temperature, placed tentatively at around 600° C., and Newhouse considers that, given slow cooling, pyrrhotites with even less nickel, would throw out the nickel completely as ex-solution pentlandite. Above 15 per cent nickel, he suggests that pyrrhotite and pentlandite form immiscible liquids at the freezing point of the pyrrhotite.

Unfortunately this work does not seem to represent the compositions it was supposed to cover. On page 294, Newhouse states explicitly that in calculating charges 60 gms. Fe were taken as required for 100 gms. FeS + $(S)_x$ and pentlandite was calculated on the *basis of 40 grams of Fe and 40 grams of Ni to 100 grams of pentlandite.* This obviously leaves only 20 grams of sulphur for pentlandite the actual composition of which is, for the formula (Fe, Ni)S, Fe, 31.75%, Ni, 32.4%, S, 34.58%. On the triangular composition diagram of the Fe-Ni-S System (Fig. 1) the section actually explored by Newhouse runs from 60Fe-40S to a composition 40Fe-40Ni-20S, provided his mixes were made as stated. Such a section crosses through the FeS field of other investigators and passes into the field of Fe-Ni alloys (Fig. 7), yet no such alloys were observed, but instead crystals resembling pyrrhotite and pentlandite were obtained. Furthermore it is difficult to reconcile Newhouse's cooling curve data with such a section. Rather, on this basis, would his section appear to run from FeS + (S_x) across the field for crystallization of FeS and into that for the low sulphur series of ternary solid solutions.

With his mixes of intermediate composition, it is clear that the charges might as well have been calculated into a sulphur-poor FeS, allowing the extra sulphur to join with the necessary Fe, Ni and S to form a ternary solid solution of the type found by other investigators.

As there is some doubt, however, as to just where the products

made by Newhouse lie on the ternary diagram it is not possible to present any sound interpretation of his results. We may note, however, the coincidence of the cooling curve breaks obtained by Newhouse at 870° C., interpreted as due to crystallization of liquid pentlandite previously separated from liquid pyrrhotite, with a similar series of breaks obtained by Urazov and Filin at about 870° C. They consider these due to a peritectic reaction between FeS + Ni crystals and liquid of composition corresponding at least to $2FeS.Ni_3S_2$ in Ni content. If Newhouse's mixtures were actually in the low sulphur region suggested, the two series of breaks may well be the same, and the suggestion of the existence of immiscible liquid pyrrhotite and pentlandite becomes unnecessary. Modifications to Newhouse's interpretation of his diagram, suggested by Hewitt, have already been referred to above. These were clearly made on the assumption that the composition of the charges was as indicated on the diagram, and do not clarify the matter.

EXPERIMENTAL INVESTIGATIONS.

Two series of investigations were made under the direction of the senior author, one in 1933 by H. F. Zurbrigg, the other in 1939 by G. L. Colgrove. The former was completed before some of the metallurgical investigations reviewed above, and before information on others and on the final formula for pentlandite had been obtained. Both series were attempts to establish the character of the FeS-NiS system and included studies of the effects of heat treatment of natural sulphides as well as an experiment to detect, if possible, any immiscibility of pyrrhotite and pentlandite liquids. In the study of natural ores, a nickeliferous pyrrhotite solid solution was detected.

First Series—FeS-NiS System.

Ferrous sulphide and prepared nickelous sulphide were mixed in various proportions, fused, quickly cooled, and the products studied by means of polished sections and x-ray powder photographs.

Preparation of Sulphides and Fusions. Iron sulphide was concentrated from a commercial product. The concentrate analyzed 63.4 per cent Fe and was accordingly fairly pure. NiS was prepared from powdered Ni and S by sealing the proper proportions in monax test tubes, placing these in a capped steel cylinder with a small amount of sulphur and heating to redness in an electric furnace. The non-magnetic product obtained resembled millerite in colour but differed from it structurally. It assayed 64.8 per cent Ni and was apparently pure NiS.

A gas furnace with a silica tube was constructed using gas and compressed air for temperatures up to 1,000° C. For higher temperatures the mixture was enriched with oxygen. Fusions were made in cups drilled in a graphite rod which was inserted in the silica tube through which a current of H_2S was passed. Each fusion consisted of about 1½ grams and with three exceptions the mixtures of FeS and NiS covered the entire range at 5 per cent intervals. Thermal measurements were made of temperatures attained in the furnace, but no cooling curves could be obtained from the small melts.

Analyses of two of the products for Ni showed the percentage had not changed during fusion. It is possible that some variations in sulphur may have occurred in the others.

Results. Examination of polished sections of the products showed five different phases present. Two of these are of little interest, one, present in the iron-rich fusions in small but fairly constant amounts, was probably an oxide of iron; the other, near the NiS end of the series occurred as fine black dendrites at the rims of the fusions and never approached 0.5 per cent of the entire surface area. The three principal phases were identified by x-ray photographs as being similar to pyrrhotite (A), pentlandite (B), and a synthetic nickel sulphide. The results are given in Table II.

Up to a composition between 15 and 25 per cent NiS, the products were homogeneous and apparently solid solutions of pyrrhotite with nickel or NiS. Between 25 and 55 per cent NiS, two phases were intergrown, phase A (pyrrhotite) showing a

TABLE II.

ZURBRIGG'S FUSIONS NiS–FeS.

Fusion NiS/FeS.	Phases Present.	Proportions.	Pattern Type.
0/100	A	—	Pyrrhotite
5/95	A	—	—
15/85	A & B	—	Pyrrhotite
25/75	A & B	B/A = 30/70	Pyrrhotite
30/70	A & B		
35/65	A & B	B/A = 37/63	Pyrrhotite strong Pentlandite weak
40/60	A & B	—	—
45/55	A & B	B/A = 68/32	Pentlandite strong Pyrrhotite weak
50/50	A & B	—	—
55/45	B (+ a little A)	—	—
60/40	B	—	—
65/35	B	—	Pentlandite
70/30	B	—	Pentlandite
80/20	B	—	Pentlandite
85/15	B	—	Pentlandite
90/10	B & C	B/C = 95/5	Pentlandite
95/5	B & C	—	Syn. NiS(?)
100/0	C	—	Syn. NiS(?)

typical herringbone structure (see Fig. 16) with respect to phase B, the "islands" of A being crystallographically continuous and surrounded by B, as shown by polarized light. From 55 to between 85 and 90 per cent NiS only one phase was present which gave a powder photograph indistinguishable from pentlandite. The third phase was questionably correlated with synthetic NiS.

No distortion of the troilite pattern was noted with increasing amounts of NiS. As a whole the pentlandite pattern remained constant except for the shifting of one line with varying composition.

Conclusions.

1. The solubility of NiS in FeS at high temperatures is between 15 and 25 per cent NiS, or between 9.7 and 16.2 per cent Ni, as compared with 13 per cent Ni given by Newhouse for FeS + xS.

2. Synthetic pentlandite, cooled fairly quickly from a high temperature, consists of a solid solution series ranging about 55NiS/45FeS by weight to about 90NiS/10FeS. The exact sulphur composition of this series though probably close to that

calculated for the charges, may be low and correspond more with the new formula $(Ni, Fe)_9S_8$. The atomic ratio of Ni : Fe in the end member of the series (55NiS/45FeS) is 11.8 Ni/10Fe and is surprisingly close to the ratio indicated by Dickson for Sudbury pentlandites.

3. The crystallization of the series was interpreted as follows: From the iron-rich members (up to 15–25 per cent NiS), pyrrhotite solid solution crystallized alone. Between 15–25 per cent and 55 per cent NiS, early dendritic crystals of synthetic pyrrhotite solid solution formed thereby reducing the FeS content of the remaining liquid until its composition had reached the point where synthetic pentlandite formed. Whether this was originally cubic or inverted to the cubic form on cooling was not clear. Using Newhouse's data, a diagram very similar to that of Urazov and Filin for the FeS-Ni_3S_2 section (Fig. 5) was prepared, though the possibility of a peritectic reaction was not considered.

4. Considering relatively low nickel-pyrrhotite ores, provided other constituents did not upset the equilibrium, the above results suggest that from a sufficiently iron-rich liquid any primary pentlandite crystallizing would necessarily have a constant composition of about 55 NiS/45FeS, and before any variation could occur in the pentlandite, the composition of the ore would have to be all pentlandite.

5. Had the papers of Vogel and Tonn and Urazov and Filin been available at the time these experiments were made, the conclusion would doubtless have been reached that their ternary solid solutions and our synthetic pentlandites belonged to one series of solid solutions with variable sulphur as well as iron and nickel.

Second Series.

The second series of experiments on the FeS-NiS system was carried out using powdered mattes which were previously made up directly to the desired composition from powdered iron, nickel and sulphur. Cooling curves were obtained by use of calibrated Pt-Pt-Rh thermocouples.

Preparation of Mattes and Fusions. Mattes were prepared in sealed pyrex tubes placed in a 3 inch-diameter, steel container sealed with a copper gasket and capable of withstanding a sulphur pressure of 400 lb. per sq. in., at 800° C. Sulphur was placed around the tubes to generate enough pressure on heating to prevent breaking.

Fusions were carried out in 1½ inch-diameter graphite crucibles fitted with a graphite lid through which a thermocouple was introduced in a porcelain protecting tube. The charge usually weighed 25 or 30 grams. The whole was encased in a 12 inch long porcelain protecting tube, also fitted with a graphite cap. Small amounts of sulphur were introduced above the graphite crucible to use up oxygen in the outer tube. All fusions were made in a heavy duty platinum-wound electric furnace capable of 1,400° C.

Possible errors in temperatures measured may be as much as 5 degrees. As a check against loss of dissociated sulphur from the molten sulphides, weights were determined before and after fusions and sulphur losses were found to average less than 1 per cent though in some cases this loss appears to have been greater. The actual line of the section investigated thus lies somewhere between the FeS-NiS and FeS-Ni_6S_5 sections of the ternary system since differences in sulphur, for instance, between 55NiS/45FeS and similar mixes in the FeS-Ni_6S_5 and Ni_3S_2 sections amount to 2.2 and 4.8 per cent sulphur respectively.

Cooling Curve Determination. Previous work by Newhouse had indicated the type of cooling curve to be expected toward the FeS end of the system. Therefore, except for several critical charges within this range, most of the curves were recorded on melts between 50 NiS/50FeS to 100 per cent by weight of NiS, and their character, *i.e.*, constant temperature, change in direction, or solid solution, was noted. The data obtained are presented in Fig. 8 with tentative suggestions regarding the interpretation. Also, to two sections across the ternary diagram, after Urazov and Filin, (Figs. 9 and 10) new points have been added.

The rate of cooling from 1,200°–1,300° C to 400° C. was

ordinarily about 160 minutes, and from 400° C. to room temperature about 15 hours. Curves were not usually carried below 400° C. Blank runs were made with powdered alumina to determine any slight deflection due to transitions in furnace materials or lag in the potentiometer used. Two fusions were quenched rapidly from high temperatures.

Identification of Phases. A longitudinal section of each fusion product was polished for microscopic examination at magnifications up to 1,200 times. A chromic acid staining solution was used on several to confirm the phases present. Up to a composition of 70 per cent NiS, only two phases were identified as synthetic pyrrhotite and pentlandite. From 70 to 100 per cent NiS, two and in some, three other phases were found, the compositions of which were not determined. The 100 per cent NiS mix yielded two phases *A* and *B*, the latter occurring both as interstitial material between crystals of *A*, and as ex-solution lamellae. Since it appeared that this part of the FeS-NiS section (from 70 to 100 per cent NiS) lies in a ternary field and no satisfactory interpretation could be made of the cooling curve data or phases, it was left for further investigation, and only those results from 100 FeS to just beyond 70NiS/30FeS are considered below.

Discussion of Phases and Textures—FeS-70NiS.30FeS. The series may be divided into three groups. Up to 5.7 per cent NiS, a homogeneous pyrrhotite type of solid solution was formed. It is to be noted, however, that No. 2 charge (5.7 per cent NiS) was sulphur-rich and may thus not be comparable with the others. The amount of pentlandite found in No. 3 (10 per cent NiS) suggests that the amount of NiS soluble in FeS is even less than indicated by No. 2 charge. Sulphur content would then be a factor in the solubility of NiS in FeS. All the other products contained both synthetic pyrrhotite and pentlandite, but in those below 50 per cent NiS, the pyrrhotite is residual following the breakdown of a former solid solution with unmixing of blades or stringers of second generation pentlandite. In those above 50 per cent NiS, no such texture was observed.

TABLE III.

No.	Composition.	Rate of Cooling.	Phases.	Texture and Remarks.
1.	2NiS–98FeS	slow	Syn. Pyrrhotite	Homogeneous at 1200×.
2.	5.7NiS–94.3FeS + *x*S	slow	Syn. Pyrrhotite	Homogeneous at 1200×. Made from natural minerals and sulphur-rich.
3.	10NiS–80FeS	slow	Syn. Pyrrhotite (Po) Syn. Pentlandite (Pn)	Groups of Po club-shaped crystals in optical continuity surrounded by Pn. Fine "ex-solution" (?) blades of Pn in most Po grains. Two generations of Pn.
4.	30NiS–70FeS	slow	Syn. Pyrrhotite (Po) Syn. Pentlandite (Pn)	Same as in No. 3. "Ex-solution" (?) blades Pn broader and less numerous, some extend to and merge with interstitial Pn.
5.	30 NiS–70FeS	rapid quench	Syn. Pyrrhotite (Po) Syn. Pentlandite (Pn)	Same as No. 4 but finer grained. (Sulphur lost.)
6.	40NiS–60FeS + *x*S	rapid quench	Syn. Pyrrhotite (Po) Syn. Pentlandite (Ph)	Immiscibility experiment (see below). Natural minerals used. Product zoned. *Inner* part—intergrowth of Po and Pn in about equal amounts, Po with ex-solution blades of Pn. *Outer* part—Pn dominant containing skeleton crystals of Po.
7.	50NiS–50FeS	slow	Syn. Pyrrhotite (Po) Syn. Pentlandite (Pn)	Similar to 5, but *no* oriented *ex-solution blades of Pn in Po.* (Fig. 16.)
8.	60NiS–40FeS	slow	Syn. Pyrrhotite (Po) Syn. Pentlandite (Pn)	Similar to 7, but more Po crystals on top than bottom of fusion.
9.	67NiS–33FeS	slow	Syn. Pyrrhotite (Po) Syn. Pentlandite (Pn)	Similar to 7, but increase amount of Pn.
10.	70NiS–30FeS	slow	95 per cent pentlandite some pyrrhotite at top, and a third Ni-rich phase at bottom.	Upper part—optically continuous Po in Pn. Lower part—third phase in irregular grains, possibly interstitial to Pn.
11.	80NiS–20FeS	slow	Three phases, one, is isotropic pentlandite the other two, not identified, are anisotropic.	Ellipsoidal texture, composed of crystallographic intergrowths of pentlandite and one unknown in a matrix of pentlandite and a second unknown. The pentlandite in ellipsoids appears to have ex-solved from an anistropic solid solution.

Throughout the series where the two phases are present the synthetic pyrrhotite occurs as groups of optically continuous, club-shaped, dendritic or ellipsoidal grains in synthetic pentlandite (Fig. 16), decreasing in amount with increasing Ni. These are similar to intergrowths obtained in the first series of experiments. Since the crystals forming first from iron-rich melts are pyrrhotite solid solutions, with higher melting points, the texture may obviously be due to early growth of pyrrhotite dendrites in the liquid and later the crystallization of a Ni-rich liquid yielding pentlandite directly or by inversion from some other form. The rounded form of some of the pyrrhotite grains may possibly be due to their partial resorption during a peritectic reaction with nickel-rich liquid as suggested by Urazov and Filin for which there is considerable support as shown below. A second possibility also considered was that the intergrowth represents the breakdown of an unstable solid solution.

Zoning in some of the fusions indicates that equilibrium was not attained in all cases. Two factors effecting the zoning may be (1) dissociation of sulphur at the surface of the melt, and (2) gravity effects. Nos. 8 and 10, showing more pyrrhotite crystals at the top of the fusion than below are highly suggestive—indicating that if these represent early crystals, they tended to float to the top of a Ni-rich liquid. Failure of these to react with the liquid to form a uniform "pentlandite" of composition about 70NiS/30FeS would account for the excess nickel sulphide which formed the third phase in No. 10. Both of these tests may be taken as favoring the peritectic reaction noted.

On the other hand, the slowly cooled 10NiS.90FeS mix yielded the typical intergrowth of synthetic pyrrohtite and pentlandite, the former predominating, whereas Zurbrigg's more quickly cooled 15NiS/25FeS mix gave a homogeneous solid solution pyrrhotite. Either the intergrowth represents the breakdown of a solid solution, or the two series of experiments are not comparable, due perhaps to a variation in sulphur. As seen below, cooling curve data favor the peritectic reaction and this second series of experiments are thus more closely related to low sulphur melts than are

the first. Under the conditions of these experiments a ternary compound close to 70NiS/30FeS in composition was formed. An x-ray powder photograph of this is indistinguishable from that of natural pentlandite, and it is presumed that the similar phase occurring in other products along with synthetic pyrrhotite is also structurally related to pentlandite. As will be seen from discussion of the cooling curve diagram, the composition of all the pentlandites obtained from various fusions should have a composition about 70NiS/30FeS, at least, at high temperatures.

Cooling Curve Data. For the section 100FeS-70NiS, three sets of cooling curve breaks were found which in general correspond with those found by other investigators (Fig. 8). Due to lack of control of sulphur content, it is not certain whether this section represents a vertical plane in the ternary system or one inclined towards the low sulphur region.

The uppermost curve *AB* includes a series of breaks which decrease in temperature from 1,178° to 978° C. for the 70/30 mix. Though somewhat lower than the points obtained by Newhouse, it is in general agreement with his. All melts cooled just below this curve *appeared* to have solidified. Breaks on the curve *AHJB* suggest a solidus for the liquidus *AB*. This together with the general character of the cooling curve results suggested the complete solidification of a series of solid solutions of a pyrrhotite type, but there is some question that complete crystallization did occur, particularly in the light of microscopic results.

The second series of breaks *CD*, also approximates that obtained by Newhouse, and ranges from 846° to 880° C. This was inferred by Newhouse as the temperature of crystallization of pentlandite, particularly since natural pentlandite melts at 878° C. at atmospheric pressure. It also agrees closely with the line *EDB* of the FeS-Ni_3S_2 section (Fig. 5), and with the line *CE* in Figures 9 and 10, after Urazov and Filin. In both cases a liquid is present. In this event, *i.e.*, if *AHJB* is not a solidus, then crystals of a solid solution (pyrrhotite) would appear to form along some curve such as *AC* or *AC'* (Fig. 8).

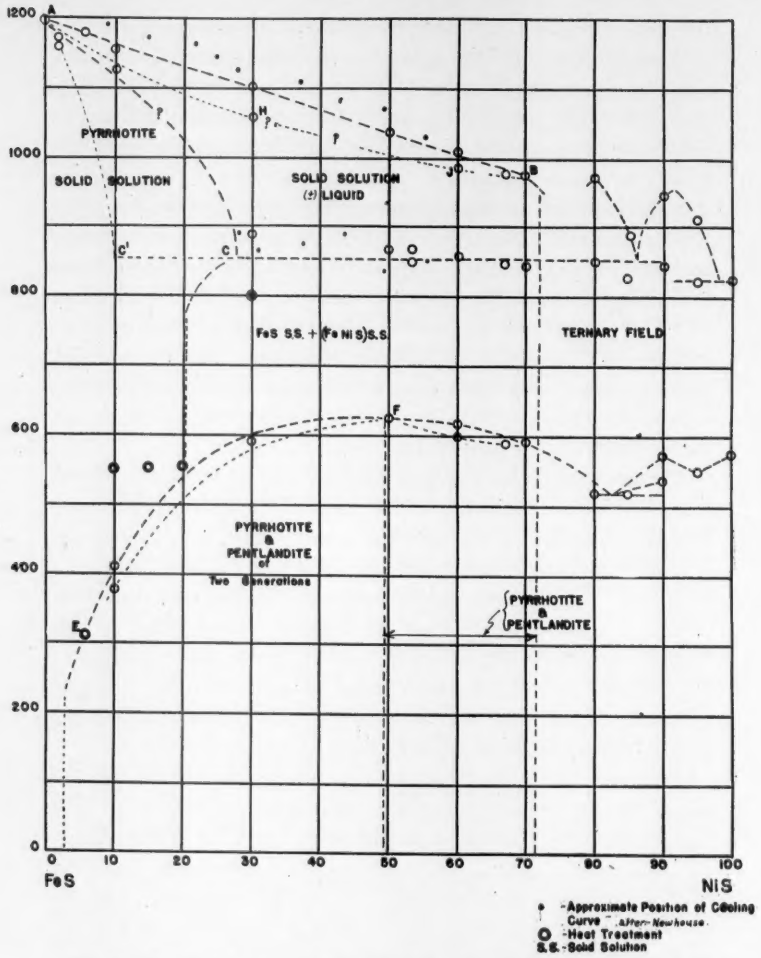


FIG. 8. Diagram showing cooling curve breaks and phases obtained from melts originally composed of mixtures of FeS and NiS after Colgrove, unpublished Master's Thesis, Queen's University. This does not represent true equilibrium conditions due likely to loss of sulphur and is open to two interpretations as explained in text.

Figures 9 and 10 are sections cutting across the ternary triangular diagram from the Fe-Ni base towards S, for the melts with 44Ni/56Fe and 56Ni/44Fe compositions respectively, after

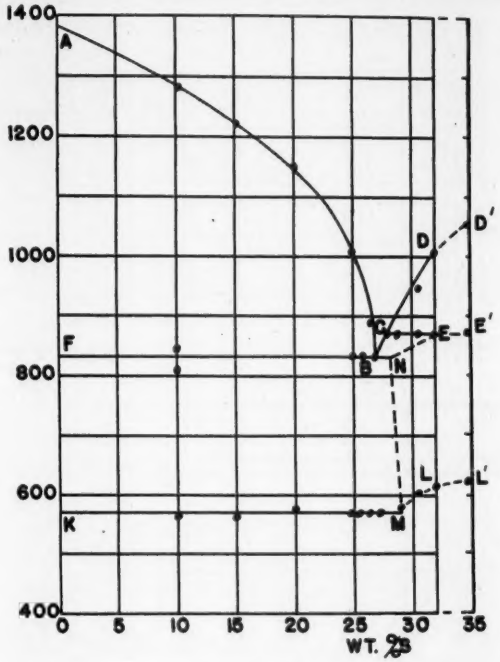


FIG. 9. Section III across ternary Fe-Ni-S diagram, Fe56, Ni44 ratio by weight, after Urazov and Filin, to which our data (Fig. 8) have been added. Fields—

ABF—crystals of Fe-Ni alloy and liquid

DCE—crystals of FeS(+ Ni)

ECBN—ternary solid solution and liquid, and product of peritectic reaction at temperature CE(870° C.)

FNMK—Fe-Ni alloy and ternary solid solution

ENML—Ternary solid solution

below *KML*—Fe-Ni alloy and ternary compound or "pentlandite." On cooling ternary solid solution ex-solves metals along *NM* and inverts at *M*.

Urazov and Filin. Our data have been added to these and show good agreement. On the right of the eutectic points *B,* in both diagrams, initial crystallization over composition *B C* yields ternary solid solution crystals, the sulphur content of which varies more widely (increasing) as the nickel content increases. For

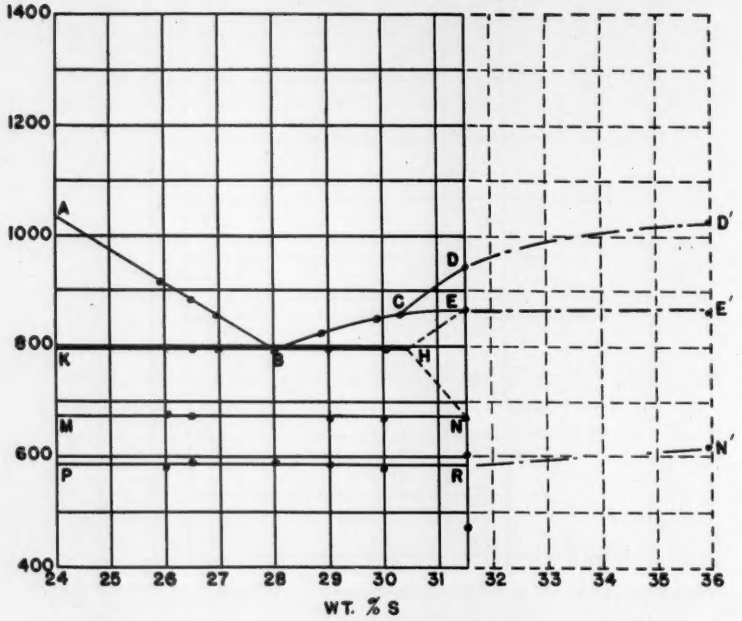


FIG. 10. Section IV across ternary Fe-Ni-S diagram, Fe44, Ni56 ratio by weight, after Urazov and Filin to which our data (Fig. 8) have been added. Fields—

AKB—crystals of Fe-Ni alloy and liquid
DCE—crystals of FeS(plus Ni)
CBEH—ternary solid solution plus liquid and product of peritectic reaction at temperature *CE*
KHNM—Fe-Ni alloy plus ternary solid solution
EHN—ternary solid solution
MN—unknown transformation
PR—transformation of ternary solid solution to ternary compound.

higher sulphur concentrations, *CD*, initial crystals, however, are recorded as of FeS (± Ni). Our points, *D'*, fit reasonably well with the curves *CD* of both diagrams. Early crystals of FeS (± Ni) are thus believed to have formed in our melts, the remaining liquid decreasing in S content and more rapidly in Fe than in Ni, until a temperature of 870° C. *ca.* (*CEE'*) at which time a peritectic reaction occurs between the crystals and liquid to form a ternary solid solution until the remaining liquid is used up. Conversely a ternary solid solution would melt incongruently at this temperature with the formation of crystals of FeS (± Ni) and a liquid richer in Ni and lower in S. As noted previously this is close to the temperature recorded by Newhouse as the melting point of pentlandite.

A third series of breaks *EFG* (Fig. 8) was also obtained with a possible maximum near the 50NiS/50FeS melt at 625° C. It corresponds with the line *ML* (Fig. 9) and the lines *FH* and *gK* of Fig. 5 which were considered by Urazov and Filin to represent the inversion of the ternary solid solution to some other form or to the ternary compound $(FeS)_2.Ni_3S_2$. X-ray analysis of our pentlandite-like phase (70/30 mix) which undoubtedly gave this third heat effect, shows its structural similarly to natural pentlandite. The inference is that this product arose from a ternary solid solution series and by inversion from some other form, and that the so-called ternary compound is related closely to pentlandite, but no explanation for the difference between natural and our high-nickel synthetic pentlandite is apparent.

From Fig. 8, it is apparent that our cooling curve data, though far from complete, if interpreted in the light of the peritectic reaction and other data given by Urazov and Filin show both similarities and certain discrepancies.

Similarities are as follows:

1. Initial crystallization of FeS(± Ni) along the liquidus *AB*, the corresponding solidus for which, is in doubt.

2. Temperature breaks along line *CD* which have not been traced to the left of *C*, and which correspond well with the temperature at which the peritectic reaction occurs.

3. Temperature breaks along line *EFG*, which are interpreted as due to an inversion of at least one of the products present, and, over the composition range *E* to *F*, the ex-solution of "pentlandite" from a pyrrhotite solid solution.

4. The formation of a ternary compound about 70NiS-30FeS in composition, corresponding with pentlandite in structure and also with the ternary compound $(FeS)_2.Ni_3S_2$ of Vogel and Tonn in Fe:Ni ratio and like it, stable down to room temperatures.

The principal discrepancy lies in the fact that the upper liquidus *CD* was not traced downward to a temperature of about 870° C. at which the peritectic reaction occurs. Furthermore, there is a strong suggestion that the corresponding solidus for this liquidus follows the curve *AHJ*, in which case a high temperature solid solution series (likely pyrrhotites) extending well across the diagram is indicated.[68] The two interpretations can obviously not be reconciled by the data at hand and our diagram cannot be taken as representing true equilibrium conditions, due likely to the progressive loss of sulphur during the experiments. It remains to be determined just what effect *constant* and even higher percentages of sulphur will have on the crystallization of this series of iron-nickel-sulphur liquids. That it has an important effect is certain as will be shown in a later paper by Colgrove.

ON IMMISCIBILITY OF LIQUID SULPHIDES.

Evidence bearing on the possibility that liquid pyrrhotite and pentlandite are immiscible or only partially miscible at the freezing point of pyrrhotite is summarized below. It is largely based on textures and is indirect.

Pro immiscibility.

1. In meteoric iron-nickel alloys, troilite (FeS) has long been known to occur in rounded, drop-like forms.

2. In pentlandite-rich pyrrhotite ores, rounded aggregates of pentlandite are surrounded by interstitial pyrrhotite (Fig. 15). The form of the pentlandite is suggestive.

[68] That a complete solid solution series exists between FeS and NiS when sulphur is constant, has been shown later by Colgrove.

3. In iron-rich melts prepared by Newhouse and ourselves, dendrites of synthetic pyrrhotite are surrounded by pentlandite. Cooling curve data admit the possibility, among others, that the sulphide liquids were partially immiscible.

The difference between these textures and that noted in (2) may simply be due to the relative amount of nickel present, and in both cases, the pyrrhotite is considered to have crystallized first.

4. Vein-like masses of pentlandite in pyrrhotite of natural ores described by Newhouse and others call for the introduction of a separate pentlandite liquid, which might have separated from an original liquid.

Evidence Against Immiscibility.

1. Vogel and Tonn [69] state that although immiscibility was expected in the FeS-Ni_3S_2-Fe-Ni system its presence could not be proven experimentally.

2. Guertler [70] found only one liquid phase in the FeS-Ni_6S_5 section.

3. Urazov and Filin indicate that, at the temperature of about 870° C. in the section FeS-Ni_3S_2, early crystals of FeS react with a nickel rich liquid to form an end member of a ternary solid solution series. This temperature agrees well with a similar break noted by Newhouse, but interpreted by him as due to the crystallization of a separate pentlandite liquid. Both thermal and textural evidence are in agreement with the alternative explanation as given by Urazov and Filin.

Experiment to Test Theory of Immiscibility.

The object of the experiment was to retain, by quenching a melt of suitable composition, any microstructures which might indicate immiscibility in the liquid state. The behaviour of other melts of a similar composition had previously shown that they were quite fluid and capable of separation. It was thus hoped that any separated liquids would be frozen in different layers.

The experiment was carried out in a graphite cylinder with a bore of ⅜ in × 2½ in. and provided with graphite screw cap, encased in a bomb prepared from "No-Kor-0-25-20" chromium-nickel steel supplied by Atlas Steel Company, Welland, Ontario, Canada.

The charge was made up from correct proportions of Sudbury pyrrhotite and pentlandite calculated to give an approximate com-

[69] Vogel and Tonn: op. cit.
[70] Guertler: op. cit.

position of 40 per cent NiS and 60 per cent FeS, by weight. The charge weighed seven grams. Several milligrams of sulphur were added to maintain a reducing atmosphere.

Heating was carried out in a platinum-wound furnace, and the temperature was raised to 1150° C. in 1½ hours and retained there for one hour. Quenching was done in salty ice water and required about one minute.

Results.

The fusion product was compact and apparently homogeneous from top to bottom with no evidence of zoning or layering. Under high magnifications it was found to consist of two phases, similar to the type of synthetic pyrrhotite-pentlandite obtained from slowly cooled melts of about the same composition. Groups of tiny club-shaped pyrrhotite crystals were in crystallographic continuity in an isotropic host. Under oil immersion lens, the pyrrhotite crystals were found in turn to be host crystals to a second generation of pentlandite.

Conclusion.

For this composition, 40NiS/60FeS, no separation of any immiscible liquids occurred in a period of one hour. The texture obtained, though finer grained, is essentially the same as in melts made at atmospheric pressure and cooled slowly.

The small quantity of visible pyrrhotite is such as to suggest that the second phase resembling pentlandite contains more than the normal amount of FeS in solid solution.

Thus, no direct evidence favors the formation of immiscible pyrrhotite and pentlandite liquids of this composition.

HEAT TREATMENT OF NATURAL ORES.

Heat treatment of natural ores by Hewitt [71] has indicated that ex-solution pentlandite will dissolve in pyrrhotite at a temperature above 425° C. and ex-solves on slow cooling from 800° C.

Heat treatment of similar ores by Zurbrigg, in an atmosphere of H_2S, strongly suggested that pentlandite dissolved in pyr-

[71] Hewitt, R. L.: op. cit., pp. 301–311.

rhotite when heated for 60 hours at 310° C. Other experiments by Colgrove corroborated data presented by Hewitt, though no runs were made below 450° C. He also found temperature breaks on cooling a melt of composition 10NiS/90FeS at 411°–377° C. Whether or not these represented the temperature of ex-solution of pentlandite was not certain.

From this data we have the suggestion that the solution or ex-solution of pentlandite in or from pyrrhotite may occur over a range of temperature, varying with the composition of the original liquid or solid solution.

TYPES OF SUDBURY ORES AND A NICKELIFEROUS PYRRHOTITE SOLID SOLUTION.

Examination of various nickel sulphide ores from Sudbury indicates that they may be classified into at least four types, according to the textural relations and relative amounts of pyrrhotite and pentlandite. In order of increasing pentlandite these are,

1. Pentlandite "veins" around all or most crystals of pyrrhotite, contacts varying from straight to feathery, the orientation of the pyrrhotite appearing to determine in part, the character of the contacts which in general are sharp, not gradational (Fig. 11). Smaller blades of "second-generation" pentlandite occur entirely within some pyrrhotite grains, as in upper left corner of Fig. 12.

2. Lamellar Ore. Murray Mine, Sudbury. Coarse pyrrhotite with basal parting contains lamellæ or "veins" of two distinct sizes, one up to 0.5 mm., wide and the other only .004 mm. Both parallel to 0001 parting. A transverse section shows the lamellar structure (Fig. 13) but a basal polished section shows dendritic, arborescent (Fig. 12), brush and flame (Fig. 14) textures. Both sizes of pentlandite may be interpreted as due to ex-solution.

3. Approximately equal amounts of pentlandite and pyrrhotite. Pentlandite is more equidimensional and over a quarter inch in diameter and not as definitely interstitial as type 1. Each contains minute inclusions of the other. Age relations are doubtful—contemporaneous or if not, some pentlandite is slightly later.

4. Pentlandite-rich ore in which pentlandite occurs as large rounded or egg-shaped masses with interstitial pyrrhotite, which appears to be

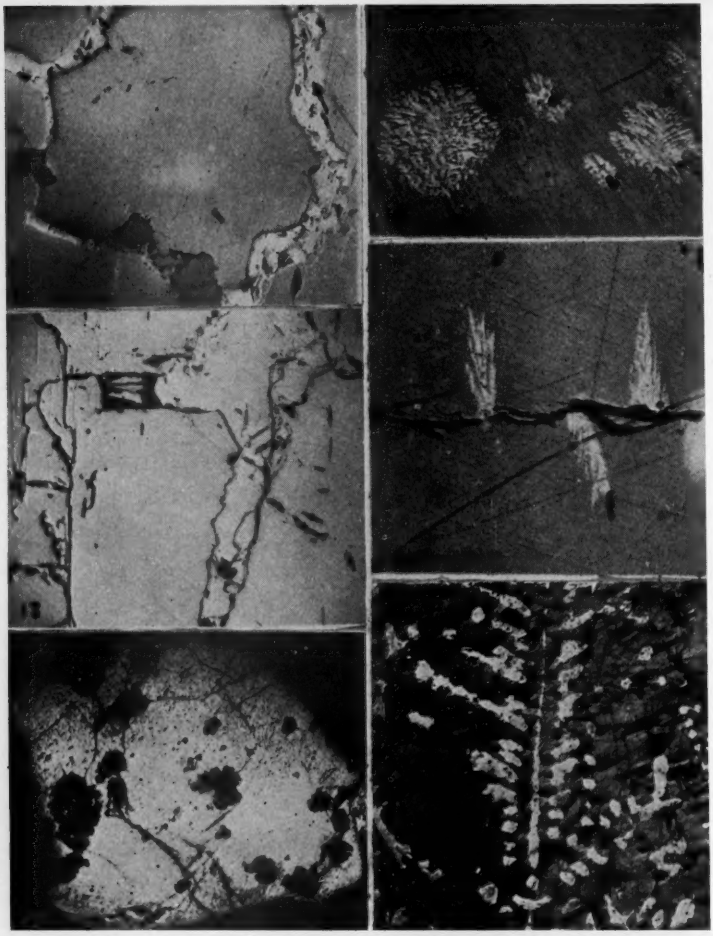


FIG. 11. Photomicrograph of light gray pentlandite surrounding grains of darker gray pyrrhotite, suggestive of cell or net texture, attributed to unmixing of a solid solution—Sudbury ore.

FIG. 12. Photomicrograph of Murray Mine ore, polished parallel to

slightly later in age than the pentlandite. The pyrrhotite, even at a magnification of 1200× is perfectly homogeneous. The pentlandite, however, shows abundant fine flecks of uniformly distributed, blocky to triangular and feathery grains of pyrrhotite, .06 to .0008 mm. in diameter and is similar to descriptions of Ehrenberg [72] and may be interpreted as due to ex-solution of pyrrhotite from an iron-rich pentlandite solid solution.

Analysis of the homogeneous pyrrhotite of ore of type 4, made on a carefully concentrated sample, gave 1.88 per cent nickel. In terms of pentlandite this would equal about 6 per cent. Lack of any visible pentlandite in this mineral is taken as an indication that it is a natural nickeliferous pyrrhotite solid solution.

From the foregoing it is suggested that the age relations of pentlandite and pyrrhotite vary according to the composition of the ore. Two generations of each may be present in some ores. The second generation in each case has been interpreted as a product of ex-solution. The first generation of each may be the product of either ex-solution or direct crystallization from a liquid. A parallel may be drawn between these ores and ilmenite-hematite ores discussed by Greig.[73] He prepared a typical phase

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basal parting of pyrrhotite, showing light-coloured dendritic, pentlandite in darker pyrrhotite.

FIG. 13. Photomicrograph of Murray Mine ore (Sudbury) showing vein-like pentlandite (light gray) traversing pyrrhotite (dark gray), and minute lamellae of pentlandite, running vertically through pyrrhotite in upper left corner. Section is polished normal to basal parting of pyrrhotite. The finer lamellae of pentlandite are less than .01 mm. wide.

FIG. 14. Photomicrograph of Murray Mine ore, showing brush or flame-like intergrowth of pentlandite (light) in pyrrhotite (dark).

FIG. 15. Photograph of a polished hand specimen of Sudbury ore showing rounded aggregates of pentlandite (dark), in pyrrhotite (light) (about ¼ natural size).

FIG. 16. Photomicrograph of a fusion made from 50NiS-50FeS, showing synthetic pyrrhotite (light) with a typical herring-bone structure in synthetic pentlandite (dark).

[72] Ehrenberg, H.: Orientierte Verwachsungen von Magnetkies und Pentlandite. Zeit. fur Kryst., 82: 309–315, 1932.

[73] Greig, J. W.: Temperature of formation of the ilmenite of the Engels copper deposits; A discussion with appendix. ECON. GEOL., XXVII: 25–38, 1932.

diagram showing the behavior of a solid solution which breaks up on cooling into two partially miscible solid solutions, each exsolving the other with lowering of temperatures and at inversion points, thus giving different generations of similar minerals over a range of temperatures. The textures exhibited by pentlandite and pyrrhotite may thus be due to immiscibility of the phases in the solid state rather than the liquid.

ON THE CRYSTALLIZATION OF NATURAL IRON AND NICKEL SULPHIDE LIQUIDS.

At least two possible modes of crystallization of non-aqueous natural liquids yielding pyrrhotite and pentlandite ores have been indicated by experimental work and a third by a textural study of the minerals themselves. The first two involve the early crystallization of a nickeliferous pyrrhotite but otherwise they differ in that one calls for the separation of immiscible sulphide liquids, the other, a peritectic reaction between pyrrhotite crystals and a nickel-(or pentlandite)-rich liquid until solidification is complete.

It has been shown that there is no positive evidence that pyrrhotite and pentlandite form immiscible liquids above the freezing point of pyrrhotite, and that the data from which this was originally inferred may be interpreted completely as due to the second method of crystallization, for which there is much more complete experimental evidence.

Brief consideration of the second and third modes of crystallization shows that either may account for many of the textural relations found in pyrrhotite-pentlandite ores. The second, according to experiments, would be necessarily typical of low-sulphur ores; the third may prevail at higher concentrations of sulphur but requires experimental confirmation.

Complete or average analyses of the sulphide portion of the common ores do not appear available so it is not possible to indicate on the ternary Fe-Ni-S diagram (Fig. 1) where their composition would fall. Actual ores, including gangue minerals assay up to 4 per cent Ni. The upper Ni limit for sulphides alone

would be about 35 per cent for rare massive lenses of pentlandite. Analyses of Sudbury pyrrhotite show an excess of sulphur to iron, but pentlandite is lower. Together, in various proportions in ores, their average should lie close to the FeS-NiS section, some below and possibly some above.

Crystallization of ores low in nickel and/or sulphur, according to the "peritectic" diagram, will account for early crystals of pyrrhotite which on cooling may ex-solve dissolved nickel to give typical intergrowths or net textures as shown by Hewitt. From liquids richer in nickel, the amount of such early crystals will be less, both by reason of the original composition, and the peritectic reaction between them and the remaining liquid. Crystallization of the remaining liquid would eventually give rise to pentlandite which could thus surround pyrrhotite and show a later age relation. Should the early crystals, as suggested by our experiments, fail to react with the residual liquid, due to floating, the liquid would therefore increase in nickel and become separated from the pyrrhotite. In other words crystallization differentiation would be effected in a manner somewhat similar to the classic example of forsterite and clinoenstatite. Depending on its composition, this liquid, on cooling might yield less pyrrhotite and more pentlandite or pure pentlandite. In any case the pyrrhotite associated with it would necessarily be earlier in age.

Figure 5, after Urazov and Filin, indicates further that on cooling, the ternary solid solution becomes richer in nickel as shown by the line *DH*. This necessitates the throwing out of FeS. May this not account for the natural occurrence of the minute ex-solved blebs of pyrrhotite in pentlandite?

According to the above method of crystallization, however, there appears no reason for any pyrrhotite, except an ex-solution type, crystallizing from a dry melt *after* pentlandite, unless it arose from an entirely new and still undifferentiated liquid. Cases cited, and our own observations on pentlandite-rich ore, in which pentlandite appears to precede the deposition of pyrrhotite are thus not easily accounted for. It is possible that other constituents in the ore-forming fluid from which these particular ores

were formed or a variation (increase) in its sulphur content may explain this reversal in the usual order of deposition.

The third mode of crystallization, suggested by recorded studies of ores and certain peculiarities in our cooling curve diagram (Fig. 8) and applicable possibly to high sulphur liquids, though differing in detail might yield much the same results as the others. Thus as in Greig's suggested diagram for such liquids as hematite and ilmenite, initial solidification of a ternary solid solution may on cooling give rise to two high temperature phases which are partially miscible in each other. Further cooling and inversions cause each to ex-solve a nickel- or an iron-rich phase, the composition depending on the temperature. From nickel-rich liquids the initial product of crystallization may invert to a pentlandite and ex-solve pyrrhotite. Such a process, however, should tend to yield pentlandites with an even higher nickel content than those found in nature, as suggested by our 70NiS/30FeS mix. Decrease of sulphur content on cooling may explain this difficulty. Lack of equilibrium between early crystals and liquid, as in any solid solution series, may explain the formation of a first crop of pyrrhotite-rich crystals and of a liquid which, though also crystallizing first to a solid solution, would by inversion, and possibly loss of sulphur, change to pentlandite. In this way primary pentlandite, as distinguished from a second generation, might form. Such pentlandite, furthermore, should always have some ex-solved pyrrhotite in close association with it.

It is apparent that the behavior of such liquids on crystallizing may be considerably affected by the content of sulphur, not only then, but during the whole cooling period as well. Further discussion on this is postponed for a later paper by Colgrove, based on more recent work with more carefully controlled sulphur.

SUMMARY AND CONCLUSIONS.

Some of the problems involved in the formation of minerals occurring in the Fe-Ni-S System are outlined, attention being directed particularly to the formation of pyrrhotite-pentlandite ores and the complex relations of these minerals. At the outset

it is noted that experimental results are applicable to ores of magmatic, and not necessarily to those of hydrothermal, origin.

Variations in composition and crystal phases of these substances are reviewed and the formula of Sudbury pentlandite is recognized as $(Ni.Fe)_9S_8$ with Ni : Fe : : 11 : 10. Except for the Lillehammer pentlandite (2FeS.NiS) the natural mineral appears to have a fairly constant composition.

A review of the metallurgical literature shows the general form of the ternary equilibrium diagram from Fe-Ni alloys up to the FeS-Ni_3S_2 section. This throws considerable light on new experimental results obtained in the vicinity of the FeS-NiS section.

The phases obtained in metallurgical studies, which are stable at room temperature, consist of FeS $\pm$ low nickel, Fe-Ni alloys, and Ni_3S_2 or Ni_6S_6, but at elevated temperatures, along the FeS-Ni_3S_2 section, FeS ($\pm$ Ni) crystals and a ternary solid solution are formed on intial crystallization. Furthermore early crystals of FeS enter into a peritectic reaction at about 870° C with a nickel-rich liquid to form an end member of the ternary solid solution series having a composition approximately 30 per cent nickel. The ternary solid solution on cooling ex-solves some FeS, forms a ternary compound $(FeS)_2Ni_3S_2$ and Ni_3S_2 according to a eutectoid reaction.

The interpretation of results obtained by Newhouse on the FeS + xS —(Fe, Ni)S (pyrrhotite-pentlandite) section is questioned, particularly since his charges apparently were much lower in sulphur than intended, and his thermal results may be otherwise construed.

The results of two series of investigations along or near the FeS-NiS section are given, one on melts in an atmosphere of H_2S, the other at atmospheric pressure of sulphur. The actual sections explored lie somewhere between the FeS-NiS and FeS-Ni_3S_2 lines due to loss of some sulphur, but they give corroboratory evidence of the "peritectic" type of crystallization of melts in this area. Phases obtained on both quick and slow cooling have been identified as pyrrhotite and pentlandite types by means of x-ray powder photographs. Other phases, likely nickel sulphides, obtained

from the Ni-rich end of the series have not been accurately determined.

The first series of quickly cooled melts made in an atmosphere of H_2S gave a nickeliferous pyrrhotite solid solution as obtained by Newhouse, an intergrowth of pyrrhotite and pentlandite, and a solid solution series corresponding with pentlandite and ranging in composition from 55NiS/45FeS to 90NiS/10FeS by weight. The former approximates the composition of Sudbury pentlandite. Whether the initial solid solution was isometric pentlandite or not, is not clear. In a general way, the results obtained fit the upper part of the FeS-Ni_3S_2 section of Urazov and Filin. They indicate that in the lower nickel part of the section, in which natural ores would fall, no variation would occur in the composition of original pentlandite until the liquid was sufficiently rich in nickel that only "pentlandite" solid solution would form.

The second series from which thermal data were obtained gave a pyrrhotite solid solution and intergrowths of synthetic pyrrhotite and pentlandite over a range of 10NiS/90FeS to 70NiS/30FeS, the latter apparently close to a ternary compound, although yielding an x-ray photograph indistinguishable from pentlandite.

Ex-solution blebs of pentlandite in pyrrhotite are found only in mixes up to 50 per cent NiS. From 70 to 100 per cent NiS, nickel sulphides were formed in addition to other phases. Cooling curve data in part agree remarkably well with that of the FeS-Ni_3S_2 section and are so interpreted. In part they also suggest early crystallization of a high temperature solid solution. Loss of sulphur may account for the failure to duplicate the ternary solid solution series obtained in the first series and it may be that the sulphur content determines the extent of the area in which the ternary compound and ternary solid solution may exist. A temperature break at about 620° C is inferred as due to a polymorphic transformation of the original ternary solid solution but the high temperature form was not determined.

An experiment to test the immiscibility theory for iron and nickel sulphides yielded negative results. In conjunction with the fact that cooling curve data on which this was based may be

more correctly interpreted according to the "peritectic" mode of crystallization, it is necessary to abandon the theory.

Acceptance of the "peritectic" mode of crystallization—for melts below the FeS-NiS section—demands that pentlandite on heating, first inverts to a member of the ternary solid solution series and then melts (at atmospheric pressure) incongruently to crystals of FeS($\pm$ Ni) and a nickel-rich liquid. Increase of sulphur will raise this melting point and may otherwise modify its behaviour.

Heat treatment of low-nickel natural ores and some thermal measurements on synthetic melts suggests that the solubility of pentlandite in pyrrhotite may vary with the temperature.

An incomplete consideration of natural ores shows that textural relations of pyrrhotite and pentlandite vary somewhat with grade or richness in pentlandite. In exceptionally rich pentlandite ore, a natural pyrrhotite solid solution (1.88% Ni) was found, opposing the idea that all pyrrhotites will completely exsolve nickel as pentlandite under natural cooling conditions. Pentlandite of this ore also shows blebs of pyrrhotite, which, if a product of ex-solution, would indicate the mineral was originally richer in FeS.

In the light of experimental work the crystallization of iron-nickel-sulphur liquids, according to the "peritectic" method, is considered adequate to explain some of the textural relations shown by natural pyrrhotite and pentlandite. It will not admit, however, of pyrrhotite being later in age than pentlandite, unless it is a product of ex-solution (and therefore really contemporaneous) or is introduced from an entirely new liquid. No suitable explanation has been found for ores which show early pentlandite followed by pyrrhotite. It may be that such have formed from a different type of liquid, perhaps hydrothermal, or an explanation may be forthcoming when the final equilibrium diagram of the Fe-Ni-S System is attained.

Mention is also made of the possibility that at the higher percentages of sulphur, iron and nickel sulphides may completely solidify as a single solid solution series, since the mineral textures

recorded are much like those of the hematite-ilmenite series for which Greig proposed a type of diagram showing partial miscibility of phases in the solid state. Further work on this aspect and on the importance of the sulphur content of the ore-forming liquids is to be recorded in a later paper by Colgrove.

ACKNOWLEDGMENTS.

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QUEEN'S UNIVERSITY,
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ON THE PRESENCE OF BORON IN BRAUNITE AND MANGANESE ORES.[1]

B. WASSERSTEIN.

ABSTRACT.

The surprising discovery that boron is a constant constituent of braunite was made spectrographically in the mineralogical laboratory of the Union Geological Survey. The common ore minerals of mangenes apart from braunite virtually carry no boron; an explanation is suggested. As braunite is an important member of the ores from the Postmasburg fields which when mined may contain 0.2 to 0.5 per cent B_2O_3 or even more, the findings may be of significance to metallurgists as steels with boron are at present receiving attention. Some ferromanganese samples and their slags were included in the spectrographic examination.

INTRODUCTION.

THE ores and ore minerals of the heavy industries have been the subject of much chemical study. When asked to check spectrographically the chemical analysis of a manganese ore which would not approximate to 100 per cent, the writer was very surprised to discover the element boron represented in the spectrum's lines. The intensity of the lines was such as to suggest that the amount present was well above the order of a "trace element" and a chemical analysis by Dr. C. F. van der Walt returned the figure 0.6 per cent B_2O_3. This ore was considered by Mr. J. E. de Villiers to be composed essentially of braunite. He provided the bulk of the selected mineral specimens from the manganese ores he was studying at that time. These samples were examined spectrographically along semi-quantitative lines with the object of determining not the precise chemical amount of this element in the minerals but rather its order of magnitude in them in order to determine its mode of distribution. For this a great many approximate analyses are preferable to a few very accurate ones,

[1] Published by permission of the Minister of Mines, Union of South Africa.

and these last become of questionable value when the extreme difficulty of isolating the individual constituents of manganese ores is remembered.

Manganese minerals have not previously been tested systematically for their boron content. Goldschmidt [2] during his geochemical studies of boron records these results:

Manganese ore, Tschiatura, Caucasus	0.005%	B_2O_3
Manganese ore, Kutais, Caucasus	0.001	B_2O_3
Braunite, Nagpur, India	0.001	B_2O_3
Asbolan, Numea, New Caledonia	0.0005	B_2O_3

They are the only determinations known from the literature to the writer and although three of them are acceptable, the fourth, the Indian braunite, is in conflict with the writer's findings and is difficult to accept, as there is not that same certainty that the specimen examined by Goldschmidt was really braunite.

The fact, that boron has been missed in the past in braunite and in manganese ores containing this mineral, must be ascribed in part to the unusualness of such an element in an ore, and in part to the difficulty of its chemical detection, especially in routine analyses. This difficulty is not shared by the spectrograph which here becomes the ideal tool for collecting many approximate results in a short space of time at little cost.

Dr. F. Meyer, General Works Manager of the local steelworks, kindly informed the writer that, according to the latest publications on boron in plain carbon steels, additions of the order 0.003 to 0.005 per cent are recommended as beneficial; that no information was available at the moment on the effect of boron on manganese steels, but that similar results to that on plain carbon steels might be expected; and lastly, that the method of introduction of the boron was still under dispute. As the question of boron in steels appears hardly beyond the experimental phase—appropriately one might say that the whole matter is in a state of flux—the results of this paper are timely and should prove of particular interest to metallurgists. It is also hoped that the results pre-

[2] Goldschmidt, V. M.: Nachr. d. Ges. d. Wiss., Göttingen, Math: Phys. Kl: 533, 1932.

sented will lead to further investigations especially along mineralogical and ore genetical lines.

PROCEDURE.

The spectrograph employed was a large Hilger Littrow type No. 478.

The usual boron doublet, 2497.7 and 2496.8, and mainly the former and more sensitive line, was used in comparing the intensities visually for obtaining the quantitative data. Copper electrodes made from wire with a diameter of 5 mm. proved very suitable as they are free from traces of boron; they are commonly used in routine work in the mineralogical laboratory of the Geological Survey. They have the advantage of cheapness for they can be used over and over again after filing the ends and cleaning them with nitric acid. They are remarkably pure, with silver as their worst contaminant. Carbon and graphite electrodes are very difficult to get under present war conditions and, as it is almost impossible to free these entirely of boron, copper electrodes become desirable for the work intended.

The ends of the electrodes were left flat and the lower one was made the cathode. It was endeavored to use the same amount of material for each exposure, which was for the first 40 seconds on arcing. It might be moré advisable to miss the first 20 seconds after which the arc burns more steadily, for contrary to expectation, the boron does not vaporize very quickly. The arc was sharply focused onto the slit whose width was 0.01 mm. the portion of the arc column nearest the cathode was photographed. The electrodes were kept 5 mm. apart; the D.C. supply was 240 V. and the amperage was nearly 5 A. The plates used were Ilford Zenith of 700 H. and D. but a few later results were obtained by using 35 mm. Kodak, Plus X nitrate film. A special film holder (made of brass) held the film's emulsion surface at the same distance from the prism as is the case with plates. The use of frequent "standard" spectra interspersed among the "unknowns" gave a ready means of comparing line intensities.

As a basis for line intensity comparisons it was desirable to have "standards" of known boron content and similar in composi-

tion to the manganese ore minerals. The analyzed material mentioned earlier provided the source of the standard preparations. Portions were diluted with pure MnO_2 to contain 0.1 per cent and 0.05 per cent B_2O_3 while another portion diluted with Fe_2O_3 gave a standard of 0.3 per cent. Under the conditions maintained there was a marked and progressive diminution of line intensity with decrease of B_2O_3 content of the standards. Using the intensity scale from 1 to 10 for the line 2497.7 the following approximate figures were obtained from a number of spectra of each standard:

7 or greater	for 0.6%	B_2O_3
4 to 6	for 0.3%	B_2O_3
2 to 3	for 0.1%	B_2O_3
1 to 2	for 0.05%	B_2O_3

From these findings it is apparent that the standards served their purpose and that this method of their preparation could be used for the determination of higher values where very approximate values were sought. Using MnO_2 and Fe_2O_3 as diluents of two samples which had given high intensities, the following results by comparison with the standards, were obtained after multiplication by a factor depending on the degree of dilution:

	Spectrographic.	Chemical (v.d. Walt).
Braunite	1.2% B_2O_3	
(Paling)	1.0 B_2O_3	
	0.8 B_2O_3	1.0% B_2O_3
	1.2 B_2O_3	
Braunite	1.2 B_2O_3	
(Beeshoek)	1.2 B_2O_3	1.1% B_2O_3
	0.8 B_2O_3	

These results show that, given big differences in line intensity in a limited range, as was experienced thus far, results of a suitable accuracy can be obtained. Furthermore, the workability of the standards as prepared, and which formed the basis for the quantitative interpretation of line intensities, is established. This method of dilution is slow, entailing multiplication of the spectra in order to arrive at a satisfactory average, for the error is greater with the amount of the diluent, so it was only used for a few samples in order to check the high values obtained.

After over 100 spectra, including many standards, had been taken under the same conditions, it was found that the higher values gave the greater uncertainty and that from about 0.5 per cent to more than 1 per cent the increase in intensity was relatively small and comparable to the variations inherent in the method. As far as the objective of this examination was concerned only values of about 0.1 per cent and over assumed any significance. For the purpose intended the following scheme of magnitudes is easily sufficient and recognizable with a tolerable amount of certainty:

0.5% B_2O_3 or >
0.3% B_2O_3
0.1% B_2O_3
0.1% B_2O_3

Intermediate values are occasionally given where the writer found that the sample could be placed in either class. It is not known what the sensitivity of the boron detection is, but it certainly lies well below 0.5 per cent B_2O_3 and does not concern us as we are not chasing it as a trace element.

RESULTS.

In the list of results the localities within the area of the Postmasburg manganese fields is given by the name of the farm only; other areas of South Africa are indicated by the district and the farm name, while overseas localities are given as fully as known.

The investigation was primarily concerned with the ores from the Postmasburg area and the accent was on the ore minerals from there but, as can be seen from the results given, the minerals cover the manganese ores mined in all parts of the world. For a better understanding of the mineral terms "partridgeite," "sitaparite" and "ferribraunite"—the last is not listed in the results—the reader is referred to Fig. 1 of Mr. de Villiers' contribution in the manganese memoir to be published shortly by the Geological Survey of the Union of South Africa.[3] Ferribraunite is not

[3] Boardman, L. G., et. el.: The Manganese deposits of the Union of South Africa. S. Africa Geol. Surv., Mem. (In preparation.)

stressed as a new mineral species, and gave results from a trace to 0.1 per cent, but it represents chemically a product intermediate between sitaparite and braunite. Recently it has been claimed that sitaparite should be classed among the discredited species;[4] this matter appears to be controversial and the name is here retained for minerals intermediate in composition between bixbyite and partridgeite. This last new mineral term has been introduced for "natural Mn_2O_3"[5] and may be regarded as a silica-free braunite to which it is closely related. In the samples examined spectrographically notable amounts of braunite were always admixed with the partridgeite owing to the difficulty of separating these two minerals.

Considering the difficulty of obtaining uncontaminated mineral components of the manganese ores, the results clearly show that *braunite and only braunite* is a carrier of boron in chemical amounts among the manganese ore minerals. Partridgeite does return somewhat high values and these are at least partly due to the presence of braunite if not wholly so; yet a limited replacement cannot be ruled out entirely. Occasionally some braunite results fall below 0.5 per cent, which can be explained by weathering, when the boron had been leached out as the psilomelanes from weathered braunite at Postmasburg indicate, or by contamination, or by an occasional poor spectrum although this was guarded against. The isolated high psilomelane result from Karreepan is due to braunite—this sample was chipped off the identical specimen which returned the high figure for Karreepan among the braunites. Apart from such contamination the psilomelanes from weathered braunites may be expected to yield higher results than those of other origin. It is interesting to note that the composite "vredenburgite," made up of jacobsite and hausmannite, contains as little boron as those two minerals individually.

The upper limit of the boron content cannot be said to have been reached, but the fact that several braunites when tested for a

[4] Mason, B.: The identity of bixbyite and sitaparite. Geol. Fören. Förhandl., 64: 117–125, 1942. Abstract in Am. Min., 9: 653, 1942.

[5] de Villiers, J. E.: A preliminary description of the new mineral partridgeite. Am. Min. (In press).

LIST OF SPECTROGRAPHIC DETERMINATIONS OF B_2O_3 IN MANGANESE ORE MINERALS.

Braunite: $3Mn_2O_3.MnSiO_3$.

	per cent.
Aucampsrust	0.5 or >
Lilyveld	0.5 or >
Black Rock	0.3
Beeshoek	0.5 or >
Beeshoek	0.5 or >
Beeshoek	0.5 or >
Beeshoek	1.1*
Mokaning	0.5 or >
Mokaning	0.6†
Gloucester	0.5 or >
Paling	0.5 or >
Paling	0.5 or >
Paling	0.5 or >
Paling	1.0*
Klipfontein	0.5 or >
Karreepan	0.5 or >
Maremane	0.5 or >
Maremane	1.2†
Mount Huxley	0.5 or >
Mount Huxley	0.5 or >
Mount Huxley	1.2†
De Nyl Zyn Oog 663 (Waterberg)	0.5 or >
Frischgewaagd 1097 (Waterberg)	0.3
Frischgewaagd 1097	0.5 or >
Genadendaal (Marico)	0.5 or >
Genadendaal	0.5 or >
Genadendaal	0.4
Genadendaal	0.4†
De Wagendrift 453 (Pretoria)	0.5 or >
De Wagendrift 453	0.3
Sitapar, India	0.3
Sitapar, India	0.3
Langban, Sweden	0.4
Langban, Sweden	0.4
Langban, Sweden	0.5 or >
Cabeça de Ferro, Brazil	0.5 or >
Cabeça de Ferro, Brazil	0.5 or >
Cabeça de Ferro, Brazil	0.8†
Thuringia, Germany	0.5 or >
Thuringia, Germany	0.5 or >

Hausmannite: Mn_3O_4.

Gloucester	Tr.
Postmasburg	0.1
Thuringia, Germany	<0.1

Hollandite: Barium-manganese-oxide.

Sitapar, India	0

* Chemical results by v.d. Walt.
† By dilution method.

Jacobsite: $MnO.Fe_2O_3$.

	per cent.
Japiesrust	<0.1
Aucampsrust	<0.1
Gloucester	Tr.
Gloucester	Tr.
Lohathla	0?

Manganite: $Mn_2O_5\,H_2O$.

Hartz, Germany	0

Partridgeites: Mn_2O_3.

Doornfontein	0.2
Doornfontein	0.3
Doornfontein	0.3
Driehoekspan	0.3

Polianite and Pyrolusite: MnO_2.

Pensfontein	<0.1
Pensfontein	0
Pensfontein	0
Black Rock	0
Mokanning	<0.1
Welgelegen (Krugersdorp)	Tr.
Bohemia, Europe	<0.1
Thuringia, Germany	0

Psilomelane: MnO_2+H_2O.

Pensfontein	0
Pensfontein	0
Cederberg Mts. (Ceres)	0?
Cederberg Mts. (Ceres)	<0.1
? ? (Riversdale)	<0.1
de Pan (Ventersdorp)	0
Karreepan	0.3
Black Rock	<0.1
Beeshoek	0.1

Rhodochrosite: $MnCO_3$.

Colorado, U.S.A.	0
Freiberg, Germany	0

Sitaparites: $(Mn, Fe)_2O_3$.

Japiesrust	<0.1
Bishop	Tr.
Sitapar, India	<0.1
Sitapar, India	0

"Vredenburgite"

(*i.e.* Jacobsite and Hausmannite).

Otjosondu 274 (Otjiwarongo) S.W.A.	<0.1

Wad.

Mooiplaats No. 69 (Pretoria)	Tr.
Kromdraai (Pretoria)	0.1
? (?)	<0.1

higher value averaged about 1 per cent, points to a rather limited replacement. This leads to the conclusion that the content of ore mined, even when very rich in braunite, is hardly likely to exceed 1 per cent B_2O_3.

BORON IN BRAUNITE.

The isomorphic replacement of Si, Al and B by each other appears tacitly accepted in mineralogical literature although no individual paper discussing this problem could be found. Their fairly close relationship to each other rather than to Mn is apparent from their position in the periodic classification of the elements. It is therefore suggested that the presence of boron in braunite is due to its isomorphic replacement of silicon within the crystal lattice. This is in keeping with the principles of isomorphic replacements and of geochemical distribution of the elements based on ionic radii enunciated so frequently by Goldschmidt and his coworkers. Mn^{4+} and Si^{4+} have similar ionic radii, whereas that of B^{3+} is somewhat removed, and hence only a limited replacement has taken place. (The valency of the boron is not known here.) As the other manganese ore minerals show no replacement by boron, which is confined to braunite, the best explanation in harmony with the observed results is that boron replaces silicon in limited and, possibly, in variable amounts according to locality.

The braunites examined come from widely separated points, in fact from four continents. No braunite tested so far has failed to show appreciable amounts of boron present while sufficient data has been collected to assert that this element is a constant companion of that mineral. It follows then that a strong positive boron test on an uncontaminated manganese mineral should help to identify the mineral as braunite, and, unless other boron minerals are present in a manganese ore, this can be shown to contain braunite by testing for boron. It might become possible to assess roughly in this way the amount of braunite in an ore.

SOME ECONOMIC ASPECTS.

To ascertain the order of magnitude of the boron content in manganese ores as exported from this country and as used here in

the production of ferromanganese, ten high grade pulp-samples of previously analyzed ores representing actual shipments were examined spectrographically with the following results:

Percentage of B_2O_3 in Postmasburg Ores	
0.3	0.4
0.4	0.4
0.5 or >	0.4
0.3	0.3
0.3	0.2

The writer is indebted to Mr. L. Moshal and Dr. W. Kupferburger for these samples and the latter was also instrumental in securing some ferromanganese and slag specimens from the electric furnaces at Vereeniging. From the ore results it can be inferred, on the basis that the Postmasburg braunites contain about 1 per cent B_2O_3, that the high grade ores commonly contain roughly 30 per cent to 40 per cent braunite.

De Villiers [6] sums up the distribution of the braunite within the manganese ores of the Postmasburg fields thus:

> Braunite is the chief ore mineral in the Eastern belt Pensfontein, Karreepan, Mt. Huxley, Maremane, the southern portion of the Western belt [Beeshoek, Doornfontein, Paling] and in the Aucampsrust area. It is also well represented in the northern portion of the Western belt [Lilyveld, Mokaning]. . . . In the central portion of this [Western] belt [Driehoekspan, Japiesrust, Gloucester, Bishop, Lohathla] it is sparingly present in the sitaparite ores.

This distribution of braunite forms a guide as to where the higher boron content ores are likely to be found.

When the slag samples were tested spectrographically, the boron lines appeared with marked intensity, but it was realized that the manganese ore standards were not necessarily applicable here; indeed a chemical checkup of such a slag by Dr. van der Walt returned the value of only 0.14 per cent B_2O_3. He failed to find any boron in a ferromanganese sample, a result supported by the spectrographic examination of four samples, which all showed the presence of traces only. Unfortunately no flue-dust sample was

[6] Op. cit.

obtainable; some material scraped off an electrode contained boron in amounts probably lower than in the slags. It is conceivable that, if any boracic acid were volatilized, it would tend to collect some distance away from the electrodes.

It is not known to what extent the haphazard samples from Vereeniging are representative, but it appears that very little of the boron is retained by the alloy, whereas in theory, the writer was told, the boron should be trapped there as borides. A certain amount does find its way into the slag with perhaps another portion joining the flue gases. The writer is left wondering whether the metallurgists could alter conditions in the furnaces so as to exploit its occurrence in manganese ores. The role of boron in manufacture falls beyond the scope of this paper but it was a matter of interest to trace this unexpected element from its source in the mineral braunite to the ore as mined and shipped, and then to its liberation (?) in the manufacture of the alloy. Attention has been drawn to the presence of this element not only in the Postbasburg ores but in some at least of the ores from Brazil and India; the Russian and Gold Coast ores are mainly made up of psilomelane and pyrolusite [7] and are therefore hardly likely to contain boron, but on the other hand "braunite is a characteristic mineral in the manganese deposits of Arkansas" [8] and there the element should be found. Unfortunately no sample was locally procurable for testing. The writer would welcome the receipt of braunite or manganese ore samples for spectrographic examination. It is quite probable that boron may yet find its way into the specifications of manganese ores and thus establish its direct economic bearing on manganese deposits.

GEOLOGICAL SURVEY,
PRETORIA, SOUTH AFRICA,
February 4, 1943.

[7] Manganese, General Information. U. S. Bur. Mines, Inf. Circ. 6729. Reprint, May 1934, pp. 4 and 7.

[8] Op. cit., p. 2.

BRAVOITE FROM A NEW LOCALITY.[1]

CHARLES ALFRED RASOR.[2]

ABSTRACT.

The discovery of a new locality for bravoite $(Ni, Fe)S_2$ has provided material for a study of this rare nickel-iron sulphide and has established the Missouri occurrence as the first in North America. The minuteness of grain size and the manner of the occurrence with pyrite precludes any determination of the optical, chemical or physical properties of the mineral. Nevertheless the remarkable zonal structure and the violet color which it exhibits in polished section agrees with that described from Mechernich,[3] Germany, and serves very well to establish its identity. Certainly, without the aid of the metallographic microscope and its accessories for high magnification, this mineral would have gone unrecognized and chemical assays would have established the pyrite merely as nickeliferous.

INTRODUCTION.

NICKEL and cobalt in ores from southeastern Missouri, for instance at Mine La Motte and other diggings near Fredericktown, were known prior to 1857 when an analysis of a sample made by Genth[4] identified siegenite ($(Ni, Co)_3S_4$) as the nickel-cobalt mineral. Brief mention of the ores and the variations in the proportion of nickel and cobalt have been noted by Neill[5] and Williams[6] in their discussions on the treatment of nickel-cobalt

[1] Published by permission of St. Louis Smelting and Refining Company and the American Cyanamid Company.

[2] Formerly Mineral Microscopist with American Cyanamid.

[3] Kalb, G., and Meyer, Emil: Die Nickel- und Kobaltfuhrung der Knottenerzalagerstatte von Mechernich. Centralbl. f. Mineral. Abt. A., p. 26, 1926.

Short, M. N., and Shannon, E. V.: Violarite and other rare nickel sulphides. Am. Min., 15: 11–13, 1930.

Schneiderhöhn, H., and Ramdohr, P.: Lehrbuch der Erzmikroskopie, Zweiter Band, Gebruder Borntrager, Berlin. Bravoit pp. 173–178, 1931.

[4] Genth, F. A.: Contribution to mineralogy. Am. Jour. Sci., 23: 419–420, 1857.

[5] Neill, J. W.: Notes on the treatment of nickel-cobalt mattes at Mine La Motte. A. I. M. E. Trans., 13: 634–639, 1884–1885.

[6] Williams, C. P.: Some points on the treatment of lead ores in Missouri. A. I. M. E. Trans., 5: 314–329, 1876.

mattes and lead ores. More complete descriptions of the mineral occurrences have been given by Buehler.[7] He stated that associated with the lead deposits of the southern portion of the "disseminated lead" district of southeastern Missouri there are extensive deposits of cobalt, nickel, copper and iron sulphides which constitute a complex ore difficult to reduce. He further stated that although this ore varied widely in composition, a general average approximates 2 per cent lead, 2 per cent copper, 1 per cent nickel and 0.8 per cent cobalt.

During times of national emergency the nickel-cobalt ores from this district have been subjected to investigation for recovery of nickel and cobalt, and, in the present emergency, tests are being made for their recovery. Samples of nickel cobalt ores from Madison County, Missouri, were sent to the Ore Dressing Laboratory of American Cyanamid Co., by the St. Louis Smelting and Refining Company for determination of an economical method of concentration.

In the course of the investigation, an iron concentrate was made and a portion was submitted to the Microscopical Department for examination to determine the reason for the presence of nickel and cobalt. Since siegenite was known as a constituent of the ore, it was assumed that a clean separation had not been made until a chemical analysis revealed the amount of nickel to be more than twice that of cobalt and in excess of that required to satisfy the formula for siegenite. These data suggested that the excess nickel might be present either as an additional nickel mineral or as nickeliferous pyrite. Its metal associations were further limited when arsenic was determined spectroscopically as present only in a few parts per million.

When the polished briquet of the concentrate was examined closely under the metallographic microscope, a pale violet mineral

[7] Buehler, H. A.: Geology and mineral deposits of the Ozark region. A. I. M. E. Trans., 58: 389–408, 1918.

Biennial Report of the State Geologist. Missouri Bur. Geol. and Mines, pp. 55–56, 1919.

. The disseminated-lead district of southern Missouri. XVI Int. Geol. Cong., Guide Book 2, Mining Districts of the Eastern States, pp. 45–55, 1932.

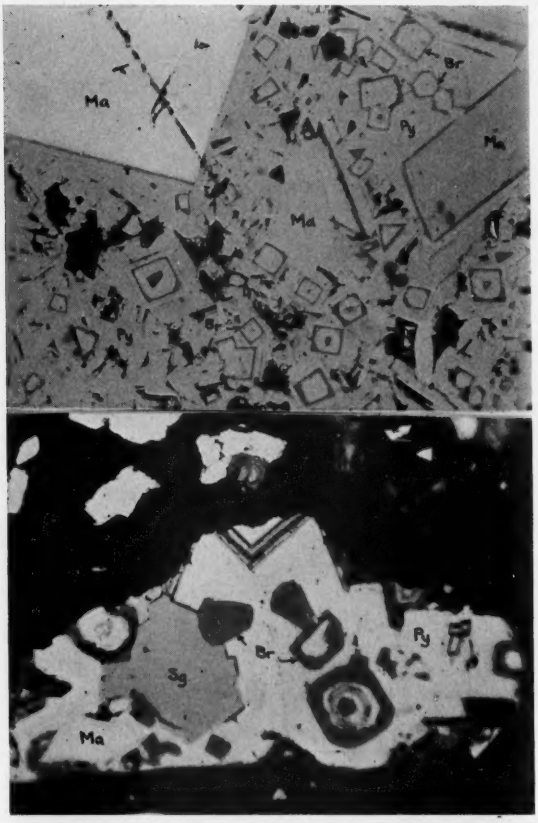


FIG. 1 (Upper). Large crystals of marcasite surrounded by grains of pyrite in which bravoite occurs as narrow zones. Ma—Marcasite, Py—Pyrite, Br—Bravoite. ×416.

FIG. 2 (Lower). Particle of pyrite in iron concentrate replaced by siegenite and bravoite. Bravoite also appears to have been later than siegenite. Py—Pyrite, Sg—Siegenite, Br—Bravoite, Ma—Marcasite. ×833.

was observed to have intimately replaced pyrite and to a minor extent siegenite. Only two minerals are recorded[8] as exhibiting a violet or lavender color, bravoite and violarite $(Ni, Fe)_3S_4$, both nickel-iron sulphides. From published descriptions[9] of the occurrence of these two minerals it was considered that the observed mineral was bravoite.

BRAVOITE.

Bravoite $(Ni, Fe)S_2$), a mineral of rare occurrence, has been identified as a constituent of the nickel-cobalt ores from southeastern Missouri and establishes that area as the first in North America in which this mineral occurs. Whereas the bravoite from Mechernich, Germany occurs in well-formed crystals up to one centimeter and can be identified by optical and chemical means, the bravoite from Missouri is so minute that crystals 30 microns or .003 centimeter in diameter are considered large. The more common occurrences are zones one half micron to five microns in thickness and definitely limit determination of any optical, chemical or physical properties. However, Schneiderhöhn says of the Mechernich bravoite:

> Die stark zonaren Bravoite sind so auffallend, dass Verweckselungen mit anderen Erzen wohl ausgeschlessen sind.

Thus the remarkable zonal occurrences in pyrite and the unmistakable violet color serve well to establish the identity of bravoite in the ores from Missouri.

Photomicrographs of the Missouri bravoite are illustrated in Figs. 1 to 7 inclusive and show the characteristic zones of bravoite in square and triangular outlines. Bravoite also follows the outlines of the mutual penetration of pyrite cubes and other diverse forms pyrite has taken on crystallizing. The reason for the intimate association of bravoite with pyrite in preference to other minerals in the ore is not known. But since it is limited to pyrite,

[8] Short, M. N.: Microscopic determination of the ore minerals. U. S. Geol. Surv. Bull., 914, 1940.

[9] Short, M. N., and Shannon, E. V.: Op. cit., pp. 13.
Schneiderhöhn, H., and Ramdohr, P.: Op. cit., p. 176.

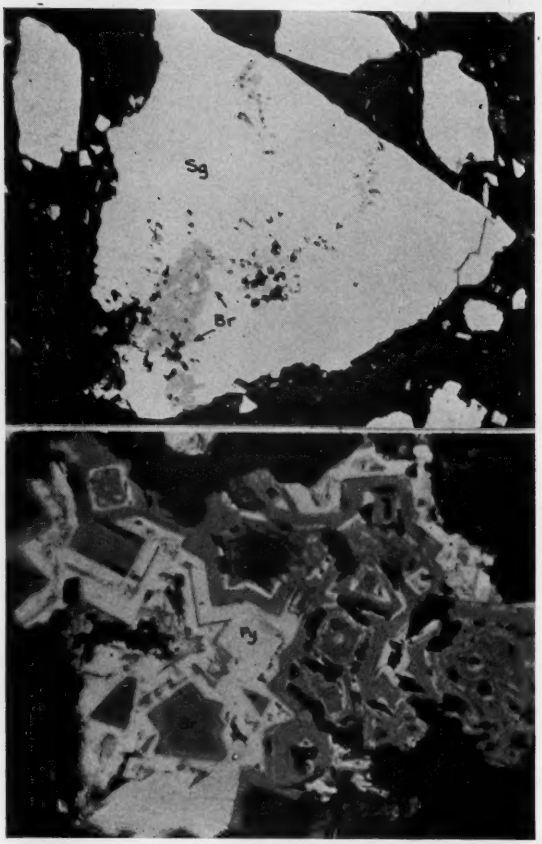


FIG. 3 (Upper). Particle of siegenite replaced in part by bravoite. Sg.—Siegenite, Br—Bravoite. ×416.

FIG. 4 (Lower). Concentric shells and nuclei of bravoite. The bands of bravoite parallel crystal faces of pyrite. Br—Bravoite, Py—Pyrite. ×833.

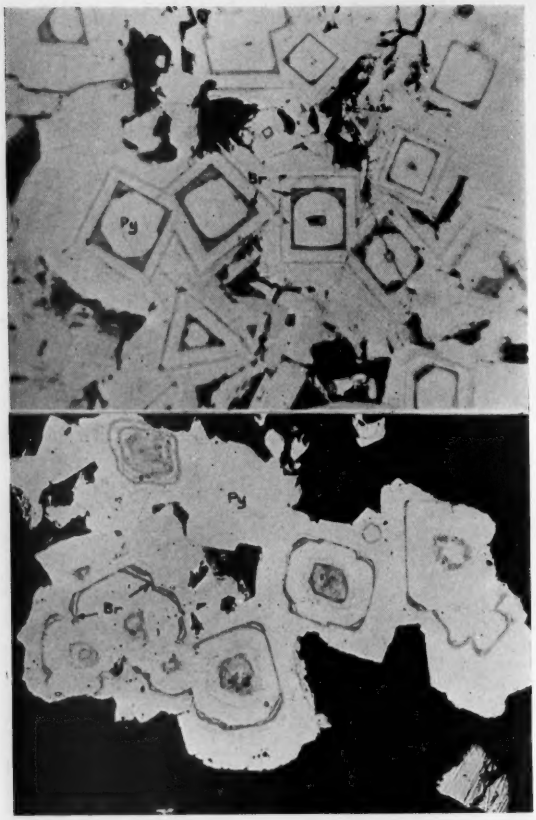


FIG. 5 (Upper). Concentric of bravoite outlining crystal faces of pyrite. Br—Bravoite, Py—Pyrite. ×833.

FIG. 6 (Lower). Another particle of pyrite outlined in part by narrow bands of bravoite. Br—Bravoite, Py—Pyrite. ×416.

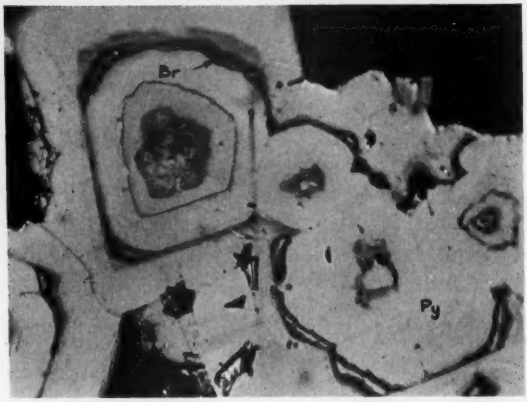


FIG. 7. Same view as Fig. 6 except at higher magnification. It would appear that bravoite had definitely replaced pyrite. Br—Bravoite, Py—Pyrite. × 833.

did it select some particular zones of weakness in the pyrite, or did it replace pyrite from the nucleus outward in rhythmical zones?

MINERAL ASSOCIATIONS AND PARAGENESIS.

Sulphide minerals in the ore besides bravoite include siegenite, linnæite (Co_3S_4), marcasite, pyrite, chalcopyrite, sphalerite and galena. The mineral assembly is rather simple and, except for the unusual occurrence of bravoite, would not be noteworthy except for the lack of such nickel minerals as pentlandite and nickel-cobalt arsenides. From microscopical observation on various mineral concentrates made in the Ore Dressing Laboratory, the paragenesis of the minerals was interpreted without the valuable aid of field observations. It is believed that all of the minerals were deposited during one period of mineralization, that is, the succession of minerals was continuous without periods of fracturing.

Marcasite is believed to have been deposited first, but the lack of

contacts with other minerals except for the straight line contacts with pyrite make its place in the order of succession confusing. Microscopical observations indicated that it was crystallizing as a coarse rather loosely coherent mass when a chemical or temperature change occurred and pyrite was deposited as minute interlocking crystals surrounding and penetrating throughout the mass of marcasite crystals (Fig. 1). Pyrite thus continued depositing until the nickel-cobalt minerals were introduced.

Linnæite and siegenite in polished section under the microscope are undistinguishable and are separated only by chemical analysis. Assays on a number of samples have shown cobalt greater in amount than nickel. There were other samples in which nickel was in greater abundance, indicating siegenite. From the numerous chemical analyses in which nickel predominated, it would seem that siegenite was the more persistent mineral, and from microscopical evidence, was introduced into the ore after the deposition of pyrite (Fig. 2).

Bravoite apparently followed the deposition of siegenite (Figs. 2 and 3) for it was observed to have replaced siegenite to a minor extent, but pyrite to a greater extent (Figs. 1, 4, 5, 6 and 7).

Although sphalerite was not observed in association with other minerals, it may have preceded or followed the deposition of chalcopyrite. On the other hand there was definite evidence that chalcopyrite replaced siegenite. There were some particles of siegenite with an anastomosing network of chalcopyrite stringers. Galena was the last mineral deposited.

RESUMÉ.

During the test work on nickel-cobalt ores from southeastern Missouri for an economical separation of the various constituents, a sample of an iron concentrate was submitted for microscopical examination to determine the manner of occurrence of the nickel cobalt. Examination of this product in polished briquets revealed the presence of bravoite and established the first North American occurrence of this rare nickel-iron sulphide in Missouri.

ACKNOWLEDGMENTS.

The writer wishes to acknowledge the courtesy of Mr. Jean McCallum, Vice President, The St. Louis Smelting and Refining Company, for permission to use data from a report describing the test work done on the ore. The writer is also indebted to Charles F. Allen and D. W. Davis, his co-workers, for suggestions during the preparation of this report.

BRUCITE IN LIMESTONE NEAR WILKINSON, ONTARIO.

I. C. BROWN.

ABSTRACT.

Brucite is present as granules, blades and needles disseminated in magnesian limestone at Wilkinson, Ontario. It is similar in character and occurrence to brucite described from limestones in other localities. In several of these occurrences brucite has been considered to have been formed by hydration of periclase resulting from decomposition of dolomite. The brucite from Wilkinson contains no remnants of periclase and is considered to be the result of a single process in which H_2O, probably in the vapor phase, replaced CO_2 of dolomite.

PREDAZZITE and pencatite, originally considered definite mineral species, were early recognized as mixtures. The identity of the constituents, however, was a matter of difference of opinion. Damour, Hauenschild, J. Roth and J. Lemberg[1] considered them to be calcite and brucite. Leneček[2] concluded the mixture to consist of calcite and hydromagnesite.

In more recent times brucite has been described from various places, including New Mexico, Nevada, and California.[3]

Still more recently considerable quantities of brucite have been found in crystalline limestones of pre-Cambrian age near Wakefield, Quebec, Pembroke, Ontario and at Rutherglen, Ontario,

[1] Lemberg: Ueber die Contactbildungen bei Predazzo. Zeit. Deutsch. Geol. Gesell., 24: 187–264, 1874.

[2] Leneček, O.: Ueber Predazzite und Pencatite. Min. und Pet. Mitt., 12: 429–446; 447–456, 1892.

[3] Dunham, K. C.: Geology of the Organ Mts. New Mexico School of Mines Bull., 11: 93–97, 1935.

Hunt, W. F., and Faust, G. T.: Pencatite from the Organ Mts. Am. Min., 22: 1151, 1937.

Callaghan, E.: Brucite deposit, Paradise Range, Nevada. Univ. Nevada Bull., 27: 27: No. 1, 1933.

Rogers, A. F.: An American occurrence of periclase. Am. Jour. Sci., 46: 581–586, 1918.

east of North Bay.[4] An occurrence similar to these, but much smaller, has been found near Wilkinson, in the township of Hinchinbrook, Frontenac county, approximately 30 miles north of Kingston. In these Canadian districts brucite occurs in small masses of crystalline limestone which are enclosed in granites or syenites, either massive or gneissoid, intrusive into the carbonate rocks. At Wilkinson the gneiss, in which the brucite-bearing limestone forms a roof pendant, is a streaked rock, pink and gray on fresh fractures, weathering to pale pink or gray. It is medium to fine grained, with a foliation that is not uniform and, in places, hardly noticeable. In general the strike of the foliation is NW–SE; the dip varies from nearly flat to vertical and both dips and strikes vary from place to place even in short distances. Commonly the surface shows intricately curved flow lines.

The light bands of the gneiss consist of mosaics of oligoclase (An_{27}) with smaller amounts of quartz and orthoclase; the dark bands contain considerable quantities of dark minerals—pyroxene, biotite, magnetite and hornblende. Lenses of dark green schistose material contain more dark minerals, especially biotite, than other parts of the gneiss, and more than half of the crystals are arranged with their longest axes roughly parallel. Most of the feldspars in these lenses are untwinned.

The limestone is coarsely crystalline. Fresh surfaces show pale gray bands, alternating with pure white ones; the rock weathers uniformly gray. Most of the limestone contains both dolomite and calcite but the proportions of them in the different bands are widely different. Many minerals are present in small quantities, of which the most common are graphite, garnet, olivine, chondrodite, phlogopite, serpentine, chlorite, hematite, pyrite, sphalerite and galena.

Analyses of specimens of limestone near lenses in which brucite occurs, as free from non-carbonate minerals as possible, and the proportions of calcite and dolomite present, are shown in Table 1.

[4] Goudge, M. F.: Magnesia from Canadian brucite. Can. Inst. Min. Met. Trans., 43: 481–505, 1940.

Osborne, F. F.: Brucite. Quebec Bur. Mines, P.M. 139, 1939.

TABLE 1.

	1	2	3	4
CaO	52.72	31.35	51.33	51.48
MgO	1.59	19.75	3.72	3.78
CO_2	43.48	46.32	44.26	42.25
$Fe_2O_3+Al_2O_3$	0.34	0.90	0.36	1.06
Insoluble	2.29	1.33	0.66	0.90
	100.42	99.65	100.33	99.47
Calcite	90.1	6.5	82.3	82.5
Dolomite	7.3	91.0	17.1	17.3
	97.4	97.5	99.4	99.8

The contact between gneiss and limestones is well exposed in many places; contact effects do not appear to be extensive. In some places a zone of coarse greenish rock, a few feet thick, made up of large crystals of mica and pyroxene, separates typical gneiss from limestone through which small quantities of chondrodite, phlogopite and similar minerals are disseminated.

THE BRUCITIC LIMESTONE.

Limestone containing brucite occurs as thin lenses in limestone that contains none. The lenses are commonly parallel to the banding of the limestone and lie a few feet above the gneiss which underlies all the limestone in this vicinity at no great depth. The largest lens is 200 feet in length by 100 feet measured down the dip and only a few feet thick.

The chief constituents of the brucite-bearing lenses are calcite, dolomite and brucite, the proportions of which vary from place to place. Other minerals present are those that occur in the non-brucitic limestone and, in addition, hydro-magnesite resulting from the alteration of brucite. Calcite and dolomite form a mosaic of closely interlocking grains, traversed by tiny stringers of dolomite, which also cut through the spherules of brucite. In places this later carbonate forms areas with micrographic texture, which are probably due to replacement of the older carbonates by the later ones. A few flakes of graphite and grains of pyrite lie between the crystals of calcite and dolomite. Rounded pink

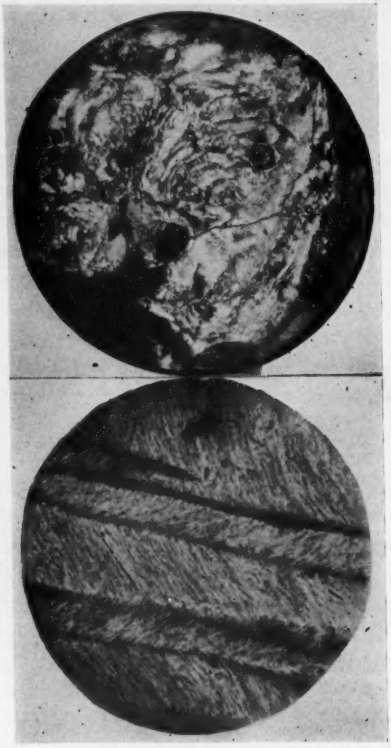


FIG. 1 (Upper). Spherule of brucite. Crossed nicols. ×25.
FIG. 2 (Lower). Detail of part of Fig. 1. Alternate bands of brucite showing herringbone structure of the fibers. Crossed nicols. ×780.

garnets with frosted surfaces are fairly common. Rounded grains and slightly elongate crystals of olivine are present and chondrodite occurs as single crystals and as small groups of rounded grains. Biotite and phlogopite lie along grain boundaries and foils of biotite follow cleavages in the dolomite of the dolomite stringers which cut the early carbonates.

Brucite is commonly visible in the hand specimens as tiny shot-

like grains with concentric structures. It is colorless, gray, yellow, or brown. In thin section two varieties are recognizable; the common fibrous type, occurring in pellets with roughly concentric onion-like shells (Fig. 1), and a clearer type, which is in plates or needles, with diamond shaped cross sections.

The layers of the spherules of the first type are made up of tiny concave scales arranged concentrically. Each scale is finely fibrous, with the fibers lying across the scale, usually at right angles to the scale surfaces and so radial to the spherule. Some, however, lie at angles as great as 45 degrees to this direction. In a few cases fibers in adjacent scales are inclined in opposite directions, giving the section a herringbone pattern (Fig. 2). The concentric structure of some grains is marked by layers of minute opaque particles, lying between the scales.

Brucite of the second type is much less abundant than that of the first. It occurs both with the spherules of fibrous brucite and as single needles or clusters of needles in the calcite and dolomite of limestones which contain no spherules. In the first case needles or plates commonly project into the outer shells of pellets thus being in part enclosed by fibrous brucite, in part by carbonates.

One good cleavage is present, in brucite of both types; in needles with diamond shaped cross-sections it is parallel to the long direction of the diamond.

The following are the optical characteristic of the fibrous variety.

Colourless to brown.

$N_o = 1.56$
$N_e = 1.58$

Interference colours of some specimens are anomalous brown.

Brucite was obtained for analysis by concentrating with Thoulet solution and picking granules from the concentrate. The sample gave the following analysis:

MgO	53.40
H_2O	23.97
CaO	4.48
CO_2 (by diff.)	3.37
$Fe_2O_3 + Al_2O_3$	4.15
Insoluble	10.63
	100.00

The calcium was probably contained in particles of calcite that adhered to brucite granules. Some of the iron is in the brucite but probably much of it is in garnet, olivine and serpentine enclosed in the granules of brucite.

Large irregular grains of pale yellow, cloudy serpentine are present in the carbonates of brucitic limestone and small rounded grains of the same type both in carbonates and brucite. The larger grains are finely fibrous, with the fibers in random orientations; the smaller ones have concentric structures. Clear, yellowish-green serpentine forms rims around, and fills fractures in, grains of other minerals—garnet, olivine, chondrodite, brucite and the cloudy variety of serpentine, and an isotropic mineral possibly spinel.

Two varieties of chlorite occur; a green variety forms rims around foils of mica and penetrates along the cleavage planes in them; flakes of a pale green, colorless variety, with low birefringence, are present in both types of serpentine.

The walls of tiny pits, from which brucite has weathered out, and the surfaces of granules of brucite exposed to weathering, are covered with thin coatings of hydromagnesite.

Several specimens of typical brucite-bearing limestone were analyzed chemically and by the Rosiwal method. For the latter the rock was stained to make it possible to distinguish calcite, dolomite and brucite. Specimens to be studied were ground to flat surfaces and immersed for one minute in dilute hydrochloric acid (1 cc. of concentrated HCl to 20 cc. of water), in which a few small crystals of potassium ferrocyanide were dissolved. Grains of brucite are stained blue almost immediately since the mineral contains some iron. After immersion specimens were washed and then placed in Lemberg's solution for 30 to 60 seconds. This stains calcite violet, dolomite remains white and the blue coloration produced in the brucite by the previous treatment is unaffected. If a specimen is left too long in the first solution, dolomite, as well as brucite is stained blue; serpentine turns a greenish blue.

The results of chemical analyses of brucite-bearing limestones is

shown in Table 2. Table 3 shows the mineralogical composition obtained by recasting. Mineralogical analyses by the Rosiwal method are shown in Table 4. Specimens 1 and 2 in Table 4 are the same as 1 and 2 in Table 2.

TABLE 2.

	1	2	3	4	5
Insoluble	1.77	1.32	2.06	2.46	1.57
$Fe_2O_3+Al_2O_3$	1.64	8.71	4.53	1.80	1.12
CaO	33.91	34.63	34.58	44.48	31.01
MgO	19.18	16.18	16.28	7.80	20.41
CO_2	40.02	34.27	40.50	43.01	46.40
H_2O	4.15	4.63	1.87		
	100.67	99.74	99.82	99.55	100.51

TABLE 3.

	1	2	3	4	5
Insoluble+$Fe_2O_3+Al_2O_3$	3.41	10.03	6.59	4.26	2.69
Calcite	35.60	47.20	31.40	59.90	4.40
Dolomite	46.00	27.30	55.75	35.10	93.80
Brucite	13.35	14.91	6.03		
	98.36	99.37	99.77	99.26	100.89

TABLE 4.

	1	2	6	7	8	9	Average
Serpentine		1				11	3
Calcite	31	56	56	41	46	46	47
Dolomite	53	32	12	30	20	22	21
Brucite	16	11	32	29	34	21	29
	100	100	100	100	100	100	100

ORIGIN OF BRUCITE.

Three modes of origin have been suggested for brucite:

(*a*) De-carbonation of dolomitic limestone with accompanying hydration.

(*b*) Alteration of serpentine.

(*c*) De-carbonation of magnesian limestones to form periclase subsequently hydrated to form brucite.

Lemberg [5] appears to have favored the first of these. He concluded that the monzonite, which is intrusive into carbonate rocks at Predazzo, furnished the heat and water necessary to effect the change of dolomite to a mixture of calcite and brucite.

He attempted to produce this result in the laboratory by passing steam through finely powdered dolomite. Carbon dioxide began to escape at 200° C. but to save time a somewhat higher temperature was used. After eight hours treatment the material was dried and analyzed.

TABLE 5.*

	1	2
CO_2	35.84	32.50
CaO	32.54	35.14
MgO	20.63	24.53
H_2O	4.80	6.81
R	6.23	1.01
	100.04	99.99

* No. 1 from Kimito, Finland. No. 2 from Predazzo, Italy. R = Disseminated silicates.

These results correspond to the following mineralogic compositions:

TABLE 6.

	Kimito.	Predazzo.
$CaCO_3$	35.84	32.50
$MgCO_3$	19.62	9.33
$Mg(OH)_2$	15.46	21.94
MgO	0.60	4.96
R	6.23	1.01
	100.01	99.99

Lemberg [6] calculated that these alterations would involve little change of volume.

It should be noted that the analyses show an excess of MgO over the amount necessary to form brucite.

[5] Lemberg, J.: Ueber die Contactbildungen bei Predazzo. Zeitschr. Deutsch. Geol. Gesell., 24: 229, 1874.

[6] Lemberg, J.: op. cit., pp. 230–238.

Poitevin and Graham [7] described brucite from Black Lake, Quebec. Fissures in massive green serpentine are lined with brucite. Both serpentine and chromite are cut by veinlets of brucite and include foliated masses of it made up of plates in radial arrangement. Other minerals present are magnetite, aragonite and hydromagnesite. Brucite is considered to be pseudomorphic after chrysotile since a part of a fiber may consist of chrysotile and other parts of hydromagnesite or brucite. This occurrence is entirely different from that at Wilkinson.

In most of the recent descriptions of occurrences of brucite the mineral is stated to have been formed by hydration of periclase. Rogers [8] described brucite from Riverside, California, which occurs as granules, the cores of which are periclase.

In the Organ Mountains, New Mexico, xenoliths of magnesian limestone, included in monzonite, have been converted into brucite and brucite-serpentine marble. Dunham [9] describes three stages of the alteration. In the first, periclase was formed from pure dolomite and forsterite from siliceous dolomite. In the second stage periclase was hydrated to form brucite and forsterite was changed to serpentine. A still later change formed lenses of magnesite from some of the brucite-serpentine marble.

Hunt and Faust [10] examined specimens of the brucite-bearing rock from the same locality. They found that the rock, in which the brucite occurs, consists approximately of 70 per cent carbonates, 26 per cent brucite and 14 per cent minor accessories, of which antigorite is the most abundant. The brucite is in granules made up of concentric whorls of fibrous and foliated aggregates. Some of the granules enclose areas of calcite and small grains of periclase. These are believed to be residual particles of the

[7] Poitevin, E., and Graham, R. P. D.: Contributions to the mineralogy of the Black Lake area, Quebec. Can. Geol. Surv. Mus. Bull., 27: 22–23, 1918.

[8] Rogers, A. F.: An American occurrence of periclase. Am. Jour. Sci., 46: 581–586, 1918.

[9] Dunham, K. C.: Xenoliths in the Organ batholith, New Mexico. Am. Min., 21: 312–320, 1936.

[10] Hunt, W. F., and Faust, G. T.: Pencatite from the Organ Mountains, New Mexico. Am. Min., 22: 1151–1160.

original periclase from which the brucite was formed. The concentric structure of the granules is considered to be due to successive stages of hydration. Variations in thickness of a single shell indicate differences in amount of water from different direction. Harker [11] described brucite-bearing rocks formed by metamorphism of dolomitic limestones by intrusives. He considered that brucite, occurring as grains with fibrous structures in mosaics of calcite, was formed by hydration of periclase, but found no relics of that mineral nor any direct evidence of the original mineral from which the brucite granules were formed. In other places metamorphism produced a rock composed of calcite, diopside and forsterite.

The brucite in the crystalline limestone at Wilkinson evidently was not formed by alteration of serpentine. Rounded grains of serpentine occur in some of the brucite-bearing limestone, but they show no traces of change to brucite. Similar grains are present in limestone which contains no brucite. As in the pencatite and predazzite of Skye, no residual periclase has been found. Other characteristics of the rock, however, are so like those of rocks in which periclase has been found with brucite, that similar modes of origin for the brucite seem to be indicated. The fibrous brucite of the granules in the limestone at Wilkinson could be considered to be the result of complete hydration of periclase, but the wedge-shaped and needle-shaped crystals of brucite, occurring as isolated individuals in the carbonate, show no evidence whatever of pseudomorphism after periclase. It seems unlikely that they could have had such an origin without showing, either in their shape or structure, some suggestion of the isometric form or cubic cleavage of periclase. Moreover the wedges and needles penetrate the margins of the granules of foliated brucite, extending into them and outward into the carbonates. They are clearly later than the granules. To assign to them a pseudomorphic origin after periclase would necessitate the assumption of two periods of formation of periclase, separated by a period of hydration.

[11] Harker, A.: The Tertiary igneous rocks of Skye. Geol. Surv. United Kingdom Mem., 1904. P. 150.

If it be assumed that brucite formed directly by elimination of CO_2 and substitution of H_2O, in a single reaction, the two types of brucite are easily explained as early and late stages of the metasomatic process.

Whichever theory is appealed to, the almost complete absence of calcium and magnesium silicates with brucite at Wilkinson requires explanation, since, normally, carbonate rocks, adjacent to later intrusives, contain large quantities of diopside and similar contact minerals. With the exception of the small amounts of mica and chondrodite, no minerals that might have come from the granite gneiss are present.

Periclase could form as an intermediate product of the alteration of dolomite to brucite, only if no water were present when the approaching magma raised the temperature of the limestone above the dissociation temperature of $MgCO_3$ for the pressure existing at that point. For, with the advent of water, hydration to brucite must have immediately occurred. Under such conditions it seems certain that, when water did come in, it would carry a considerable amount of material from which silicates would form. On the other hand, if de-carbonation and hydration be assumed to have occurred simultaneously, aqueous vapors may have been the forerunners of the magma and may have been capable of carrying little in solution. Thus little but water may have reached the area of brucite formation.

SUMMARY.

Brucite at Wilkinson, as at other localities in Ontario, occurs in magnesian limestones near the margins of great bodies of granite or granite gneiss, intrusive into the limestone. The brucite-bearing limestone consists of a mosaic of calcite and dolomite occurring in different proportions at different places. The brucite occurs as a foliated type in granules, and as slightly later individual needles and blades.

Brucite has formed at the expense of dolomite—the calcium of the dolomite going to form calcite. Hence some calcite is

present in all occurrences of brucite and, in places, little dolomite is left.

Brucite occurs at Wilkinson in associations very similar to those at Riverside, California, where it seems clearly to be secondary after periclase, and to those on the island of Skye where it is assumed to have completely replaced periclase. The Wilkinson brucite, however, is thought to have been formed by a single reaction in which H_2O replaced the CO_2 of dolomite to form calcite and brucite.

The paucity of contact metamorphic silicates is attributed to formation of brucite by steam, preceding the advancing magma, and carrying little material in solution.

QUEEN'S UNIVERSITY,
KINGSTON, ONTARIO,
February 16, 1943.

DISCUSSION AND COMMUNICATIONS

CALCITE–DOLOMITE STAINING TESTS.

Sir: John Ridge, in his paper on "The genesis of the Tri-State zinc and lead ores,"[1] states in a footnote on page 299, with respect to the replacement of limestone by dolomite, that "Dolomite was tested for in this investigation by the use of Lemberg's solution. (See Fairbanks, E. E.: A modification of Lemberg's staining method. Amer. Min. 10: 126–127, 1925.)"

It has been my experience that the dolomite of the breccia orebodies of the Joplin region, because of its marked physical characters, may be readily identified with certainty by inspection alone, both in the field and in the hand specimen, and almost without exception, in thin sections as well. For this reason, it had never occurred to me to test for dolomite in orebody specimens with a stain. I had used the common and more certain, although less rapid, chemical test for magnesium, for distinguishing fine-grained dolomite and magnesian limestone from non-magnesian limestone in the drill cuttings of deep wells, below the Grand Falls chert, but the dolomite of the orebodies above this chert is so distinctive, both to the naked eye and under the microscope, that a test of any sort had seemed unnecessary. However, after reading Ridge's statement and his conclusions with regard to replacements and mineral paragenesis, which differed considerably from my own conclusions, I made a few tests of thin sections of known character, using, as he did, the Lemberg formula as modified by Fairbanks. The results, however, were neither well defined nor distinctive. Another dye was then tried in place of the hematoxylin but with no better results. Later, I tried the ferric chloride method of staining[2] and found the contrasts obtained by

[1] Econ. Geol. 31: 298–313, 1936.

[2] Keller, W. D., and Moore, G. E.: Staining drill cuttings for calcite-dolomite differentiation. A. A. P. G. Bull. 21: 949–951, 1937.

this method to be definite and entirely satisfactory but the results, with regard to mineral identification, were still not what had been expected.

Thin sections were not used for these later tests. Instead, the fine sand of selected samples of dolomite and limestone, which, after crushing, passed a 60-mesh screen but remained on a 100-mesh screen, was used. In making the tests, a small amount of the sand was immersed for five or ten seconds in a two and one-half per cent solution of ferric chloride. After washing, the sand was then immersed for ten seconds in an ammonium sulphide solution saturated with H_2S. This was followed by a final washing. All of the tests were duplicated, there being no observable difference, however, in the results of the two series. The material used was (1) limestone from the quarries at Carthage, Mo., (2) typical, fresh gray dolomite containing no calcite, from a mine near Joplin, and (3) pure pink dolomite crystals, like the dolomite used for the analysis given on page 296 of U. S. Geological Survey Bulletin No. 591. The limestone used in the test acted in the normal manner and all of the sand grains were stained black. In the case of the gray dolomite, however, which should have remained uncolored, more than sixty per cent of the grains were wholly blackened. A part of the remaining grains became grayish and each grain of the rest was partly gray and partly black. Even the pink dolomite reacted somewhat with the reagents and three or four per cent of its grains were blackened, the rest staining a greenish gray. The ammonium sulphide, when used alone with the gray dolomite, caused a decided darkening of all the grains, although it had no noticeable effect on the grains of the Carthage limestone.

In explanation of these results, it may be stated that, in every mine of the Joplin district examined by me, there was at least a slight alteration of the orebody, and many of the orebodies were considerably altered. The evidence indicates that the cause of this alteration was a very weak solution of iron sulphate, probably both ferrous and ferric, acting over a long period of time. It seems probable that it was the effect of this action that caused

the abnormal reaction of the dolomite in the ferric chloride test. Whatever the cause, however, it is evident that staining methods cannot safely be used for distinguishing dolomite from calcite in the ore deposits of the Joplin region.

W. S. Tangier Smith.

Menlo Park, California,
February 16, 1943.

REVIEWS *

The Dynamics of Faulting and Dyke Formation, with Applications to Britain. By E. M. ANDERSON. Pp. xii + 191; Figs. 38. Oliver and Boyd, Edinburgh and London, 1942. Price, 15 shillings.

Britain is classic geologic ground, with many kinds of features that are well known through long study. Faults and dikes are particularly well represented, on large and small scales, and are accurately mapped on excellent sheets of the Geological Survey. The island therefore presents an exceptional opportunity for a synthetic study, with emphasis on the genesis of faults and dikes in sets or systems. Dr. Anderson's long experience with structural problems has made him exceptionally well qualified for such a study.

The reasoning is partly deductive, but constant reference to actual field examples furnishes a strong inductive check on theory. Dynamic conditions in the earth's crust are referred to an ideal standard of reference, or *standard state*, which is defined as "a condition in which the lateral pressure from all sides increases steadily with depth, so as to be everywhere equal to the vertical." Both faulting and dike formation reflect some departure from the standard state, by increase or decrease in pressure along one or more of the principal stress axes. Since faults and dikes commonly show a close relationship in their orientation, some geologists believe there is a dynamic relationship between them. However, faulting results from failure under shearing stress, whereas dikes follow fractures that are formed or opened by tensile stress. The tension need not be regional. Probably all dikes are forced up under powerful pressure, but there is tension across the thin edge of the advancing wedge, continuously extending the fracture. Many dikes follow preëxistent faults, since a ready-made break offers the easiest escape unless the greatest horizontal pressure is nearly at right angles to the old fracture plane.

In his analysis of faulting the author adheres consistently to "Navier's principle," first advanced more than a hundred years ago and repeatedly reannounced, under other names, by later workers. This principle states

* Books noted under *Reviews* and *Books Received* may be ordered through the Economic Geology Bookshop, M. M. Leighton, Urbana, Ill., but orders for official reports and single copies of Journals should be sent directly to their publishers.

that under shearing stress conjugate fracture planes form, not midway between the directions of greatest and least pressure, but at an angle appreciably less than 45 degrees on either side of the axis of greatest pressure. This principle, long accepted by mechanical engineers and amply supported by experimental evidence, was explained by Navier on the basis of a "coefficient of internal friction" which he regarded as constant for a given material. Mohr and others elaborated but did not fundamentally change Navier's statement of the principle. Anderson's clear explanation of this subject can be read with profit in this country, where there has been much confusion on the subject of fractures due to shearing. Probably this confusion has resulted largely from the widespread habit among geologists of invoking the strain ellipsoid concept in attempts to analyze structural failure of every kind. Anderson does not mention the strain ellipsoid, and yet there is no difficulty in following his analysis of dynamic conditions in three dimensions. The space relation of conjugate shear planes is determined by two simple principles: the acute angle between the planes is bisected by the axis of maximum pressure, and the planes intersect along the axis of intermediate pressure. Thus thrust faults characteristically have dips much lower than 45 degrees, "transcurrent" (strike-slip) faults tend to be nearly vertical, and normal faults generally have steep dips.

In the reviewer's opinion some of Anderson's generalizations are far too sweeping. The chief cause of this weakness lies in an incomplete inventory of forces that are responsible for crustal deformation. According to Anderson these forces act either nearly horizontally or nearly vertically, and the only vertical force to be reckoned with is gravity. It is a commonplace of geology that plateaus and large mountain blocks have been uplifted. Whatever the origin of the forces, their differential action must have set up shearing stresses. Many large normal faults in and adjoining plateaus may have resulted in this way. Anderson's analysis of normal faulting, however, allows no exception to the brief pronouncement, "The greatest pressure is then the vertical pressure which is due to gravity." Moreover he has no place in his classification for high-angle reverse faults, although in some regions large faults of this kind, with dips ranging from 50 to 80 degrees, are common. Anderson's neglect of these important features perhaps reflects their scarcity among the faults known in Britain, but apparently results also from his failure to consider lifting forces in his basic theory. He states that "fault-breccias frequently occur along normal and transcurrent faults, but not in association with thrust planes," and offers an explanation based on theoretical considerations. In the reviewer's experience, however, the most impressive of all fault breccies occur in the basal portions of great thrust plates, as

illustrated by several examples in southern Nevada and eastern California. The apparent contradiction in observed evidence may have a ready explanation. Many of the plates preserved in southwestern United States were driven over irregular topographic surfaces, whereas Anderson's examples may represent deeper parts of thrusts, below the contemporary land surfaces. Another statement that seems too bold is the following: "It follows from the dynamical theory that thrust planes and normal faults can never occur in association." Some thrust plates riding forward on uneven surfaces may be subjected to differential uplift and local torsion, with resulting failure by normal faulting. The reviewer believes he can cite illustrative examples.

The author keeps his terminology commendably simple, in a subject that is burdened with a multiplicity of terms, some of them used with diverse meanings. Perhaps mild protest is in order at his adoption of *transcurrent* fault as the generic term "for members of the class which are distinguished by lateral movement, with inclinations which, according to theory, are nearly vertical." This term has been used, logically enough, to designate faults of this kind which intersect at large angles a regional structure pattern, including fold axes. Some of the examples cited—as those in Pembrokeshire—conform to this description. Many others used as illustrations traverse unfolded rocks and do not seem to merit the term *transcurrent,* since they cut across no visible structural pattern. Why isn't *strike-slip* fault the most satisfactory generic term, since it is free from the undesirable connotations and double meanings that beset many others in our abused terminology of faults?

After these critical comments, chiefly on matters of detail, the reviewer returns to hearty indorsement of the book as a whole. American readers will find in it much new interesting factual material from England, Wales, and Scotland. Deductions of structural principles are clearly reasoned and are supported by a wealth of illustrations from the field. Finally each of the eight chapters contains a substantial list of references to pertinent literature, for which every serious reader will be grateful.

CHESTER R. LONGWELL.

Landscape. By C. A. COTTON. Pp. xviii + 301; Figs. 214; Pls. 45. The University Press, Cambridge; Macmillan Co., New York, 1941. Price, $4.75.

Probably no single land unit has been so thoroughly described by an individual as has New Zealand. Primarily a geomorphologist, C. A. Cotton began his descriptions in 1912 with *Notes on Wellington Physiography.* Some 20 publications on New Zealand appeared under his name between this early work and his excellent text, *Geomorphology of New Zealand,*

presented in 1926. The present volume, however, is certainly not confined to land forms of New Zealand, although the author finds within his country many examples of described features.

A student and ardent disciple of W. M. Davis, Professor Cotton adheres to a method of deductive analysis in describing and classifying land forms. An early chapter on mass wasting is followed by numerous chapters on the study of rivers and related phenomena. Later chapters are devoted to peneplains, fossil land surfaces, effects of base level change, fault features and limestone landscapes. The text is amply illustrated throughout by the author's pen sketches, but unfortunately the 86 excellent reproductions of photographs are restricted to the final pages.

As the title indicates, the text material deals with landscapes as developed by the processes of normal erosion. Cotton, however, does not burden the reader with undue terminology and description, but, rather, emphasizes the principles underlying the formation of land forms. This is a systemmatic study and the subject matter is presented in a readable and interesting fashion.

RALPH E. DIGMAN.

The Origin of the Carolina Bays. By DOUGLAS JOHNSON. Pp. xi + 341; Figs. 46. Columbia University Press, New York, 1942. Price, $4.50.

This volume, number four of the Columbia Geomorphic Studies, is concerned with a problem that has held considerable popular as well as geologic interest since aerial photographs presented the magnitude and complexity of the "Carolina bays." The author interested himself in the problem a number of years ago and his protracted investigations since that time have resulted in an accumulation of data that aptly fit him for the task of presenting the problem and suggesting the most tenable solution. His manner of presentation is such that the layman will receive a full understanding of the problem and its complications, and the scientific audience will delight in the approach and find an authoritative explanation of this extraordinary land form. The brilliant air photographs and understandable diagrams will be considerable aid to both.

The "bays" of the Carolinas and adjacent states are shallow depressions a few hundred feet to several miles in length and occur by the tens or hundreds of thousands on the coastal plain of this region. The symmetrical oval outline of the basins, their uniform northwest-southeast orientation, and the development of sand ridges on their southeastern rims present an unusual problem. An explanation of origin involving bombardment by a shower of meteorites received general acceptance and,

indeed, a text on meteors and meteorites contained as its frontispiece a photograph of several of the bays.

After an introduction to the nature of the problem, Johnson discusses the meteoric explanation and various hypotheses involving terrestrial origin. In chapter 9 he presents his own "hypothesis of complex origin" involving artesian, solution, lacustrine, and aeolian agents. Formation of the basins is attributed to excavation by upward-moving artesian water with removal by ground water near the surface. The orientation of the bays is considered due to relative constancy in direction of flow of the waters. The rounded outlines are held to be due to uniformity of flow of loose sand toward the locus of greatest removal. The apparent infilling of many of the bays by peat and swampy soil is ascribed to lowering of the water table and encroachment of vegetation. The sand rims are considered due to action of prevailing winds. In the final chapter, the author considers possible weaknesses of his hypothesis and notes similar oval lakes in other regions.

The excellent presentation of this very fascinating land form is a credit to the author and the hypothesis advanced appears competent to explain all the unusual features of the basins.

RALPH E. DIGMAN.

BOOKS RECEIVED.

RALPH E. DIGMAN.

Boom Copper. ANGUS MURDOCH. Pp. 255; Pls. 15. Macmillan Co., New York, 1943. Price, $3.00.

Aerial Photographs and their Application. H. T. U. SMITH. Pp. xiv + 372; Figs. 51; Pls. 62. D. Appleton-Century Co., New York, 1943. Price, $3.75.

Geology of Kentucky. ARTHUR C. MCFARLAN. Pp. xxviii + 531; Figs. 42; Pls. 118. University of Kentucky, Lexington, 1943. *Professor McFarlan, revising and enlarging A. M. Miller's Geology of Kentucky published in 1919, began work on this volume in 1932. Its timely publication helps celebrate the seventy-fifth anniversary of the University of Kentucky. The contents of the volume are divided into six parts, stratigraphy, structural geology, outline of historical geology, regional geology, natural and scenic features, and mineral resources. A 66-page bibliography adds to the value of the book as a reference to the geology of Kentucky. The numerous plates include topographic sheets, structure sections, and geographic charts. Halftone pictures show scenic features and important outcrops.*

Oil and Gas Resources of Cass and Jackson Counties, Missouri. JOSEPH R. CLAIR. Vol. XXVII, Second Series. Pp. 207; Figs. 14; Pls. 7. Missouri Geol. Surv. and Water Resources, Rolla, 1943. *A discussion of the stratigraphy, structural geology, and economic geology*

of these two counties in western Missouri is followed by recommendations for further shallow development and suggestions for deeper prospecting. Included in the appendix are well water analyses, extensive data of deep wells and Cherokee wells in the two counties, and typical well logs. "In this report the writer has attempted to bring together all available information both surface and subsurface and thereby designate areas in which future development may be expected."

Montgomery County Mineral Resources. R. R. PRIDDY AND T. E. MCCUTCHEON. Pp. 115; Figs. 18; Maps 2. Mississippi Geol. Surv., Bull. 51, University, 1943.

Coal Beds of Western Carroll County and Coal Beds in Southeastern Mahoning County. R. E. LAMBORN. Pp. 33. Ohio Geol. Surv., 4th Ser., Bull. 43, Columbus, 1942.

Los Yacimientos de Wolfram de Bolivia. FEDERICO AHLFELD. Pp. 108; Figs. 23. Sección de Geología de la Dirección General de Menas y Petroleos. La Paz, Bolivia, 1942.

Brazil Departamento Nacional da Produçao Mineral, Rio de Janeiro, Brazil.

Plantas Fosseis do Neo-Paleozoíco-do-Parana e Santa Catarina. CHARLES B. READ. Pp. 102; Pls. 8; Map 1. Div. de Geol. e Min. Mon. XII, 1941. *A discussion and list of fossil plants from the late Paleozoic of southern Brazil. Written in Spanish and English.*

O Novo Distrito Hidromineral de Passa Quarto. A. GIROTTO. Pp. 72; Figs. 6; Pls. 31. Bol. 3, 1941.

Geologia de Mafra. P. F. DE CARVALHO AND OTHERS. Pp. 41; Pls. 7. Div. de Geol. e Min. Bol. No. 105, 1942.

Estratigrafia do Reconcave da Baia. J. L. DE MELO, JR. Pp. 62; Figs. 5. Div. Geol. e Min. Bol. No. 110, 1942.

Relatorio. L. J. DE MORAES. Pp. 50. 1942. *Report of explorations, discoveries, and important minerals of Brazil by the Director General of the Department of Mineral Production.*

Estratigrafia da Serie Bambui em Sete Lagoas, Minaes Gerais. E. P. SCORZA. Pp. 16; Figs. 4. Div. de Geol. e Min. No. 23, 1942.

Ouro no Bloco do Butiá. E. A. TEIXEIRA AND V. LEINTZ. Pp. 81; Figs. 2; Pls. 8. Div. de Fomento da Producao Min. Bol. 50, 1942.

Ouro na Serra de Jacobina. H. C. A. DE SOUZA. Div. de Fomento da Producao Min. Bol. 51, 1942.

Manganes na Baia. H. C. A. DE SOUZA. Pp. 63; Figs. 23. Div. de Fomento da Producao Min. Bol. 52, 1942.

Higiene das Minas de Ouro. Silicose e outras doencas dos Mineiros-da-Passagem (Minas Gerais). C. M. TEIXEIRA AND OTHERS. Pp. 113; Figs. 9. Div. de Fomento da Producao Min. Bol. 53, 1942.

Cromo na Baia. H. C. A. DE SOUZA. Pp. 110; Figs. 17; Pls. 28. Div. de Fomento da Producao Min. Bol. 54, 1942.

Codigo de Minas. Pp. 102. Div. de Fomento da Producao Min. Avul. 46, 1942.

O Codigo de Minas e o incremento da Mineracao no Brasil em 1940. GLYCON DE PAIVA. Pp. 38; Figs. 3. Div. de Fomento da Producao Min. Avul. 47, 1942.

Como Requerer Pesquisa de Jazida Mineral. Pp. 29; Fig. 1. Div. de Fomento da Producao Min. Avul. 48, 1942.

Captacao das Fontes de Sao Lourenco. J. F. DE ANDRADE, JR. Pp. 40; Figs. 4; Pls. 9. Lab. da Producao Min. Bol. 4, 1942.

Investigacoes Micro-Quimicas. FRITZ FEIGL AND OTHERS. Pp. 170. Lab. da Producao Min. Bol. 5, 1942. *Abstracts of the several articles included are written in Spanish, French, German and English.*

U. S. Geological Survey. Washington, 1942–1943.

Bull. 900–J. Subsurface Geology and Oil and Gas Resources of Osage County, Oklahoma. N. W. BASS, H. B. GOODRICH, AND W. R. DILLARD. Pp. 20; Figs. 3; Pls. 3. Price, 60 cents.

Bull. 900–K. Subsurface Geology and Oil and Gas Resources of Osage County, Oklahoma. Part 11. N. W. BASS. Pp. 44; Figs. 3; Pls. 8. Price, 45 cents.

Bull. 926–D. Geology of the Portage Pass Area, Alaska. F. F. BARNES. Pp. 24; Fig. 1; Pls. 9. Price, 20 cents.

Bull. 934. Phosphate Resources of Florida. G. R. MANSFIELD. Pp. 81; Fig. 1; Pls. 8. Price, $1.00.

Bull. 436–J. The Tin-Spodumene Belt of the Carolinas (Prelim. report). T. L. KESLER. Pp. 21; Figs. 2; Pls. 5. Price, 50 cents.

Bull. 936–L. The Three Kids Manganese District, Clark County, Nevada. C. B. HUNT, V. E. MCKELVEY, AND J. H. WIESE. Pp. 19; Figs. 5; Pls. 3. Price, 30 cents.

Bull. 936–P. Vanadium Deposits of Colorado and Utah (Prelim. report). RICHARD P. FISCHER. Pp. 31; Figs. 5; Pls. 5. Price, 30 cents.

Bull. 938. Bibliography of North American Geology, 1940 and 1941. EMMA M. THOM. Pp. 479. Price, 50 cents.

Bull. 939–C. Geophysical Abstracts 110, July–September, 1942. W. AYVAZOGLOU (Compiled). Pp. 98. Price, 10 cents.

Prof. Pap. 197–D. The Basin and Range Province in Utah, Nevada, and California. THOMAS B. NOLAN. Pp. 55; Figs. 4; Pls. 2. Price, 15 cents.

Prof. Pap. 197–E. Some Standard Thermal Dehydration Curves of Minerals. P. G. NUTTING. Pp. 19; Figs. 9. Price, 5 cents.

Prof. Pap. 197–F. The Action of Some Aqueous Solutions on Clays of the Montmorillonite Group. P. G. NUTTING. Pp. 16; Figs. 10. Price, 10 cents.

W. S. P. 844. Floods of March 1938 in Southern California. HAROLD C. TROXELL AND OTHERS. Pp. 395; Figs. 40; Pls. 26; Tables 32. Price, $1.25.

W. S. P. 922. Surface Water Supply of the U. S. 1941. Part 2, South Atlantic Slope and Eastern Gulf of Mexico Basins. GLENN L. PARKER AND OTHERS. Pp. 427; Pl. 1. Price, 75 cents.

W. S. P. 924. Surface Water Supply of the U. S. 1941. Part 4, St. Lawrence River Basin. GLENN L. PARKER AND OTHERS. Pp. 185; Pl. 1. Price, 25 cents.

W. S. P. 926. Surface Water Supply of the U. S. 1941. Part 6, Missouri River Basin. GLENN L. PARKER AND OTHERS. Pp. 471; Pl. 1. Price, 60 cents.

SCIENTIFIC NOTES AND NEWS

A. R. KINKEL, JR., formerly chief geologist of the Buffalo Ankerite Gold Mine, South Porcupine, Ontario, has recently joined the U. S. Geological Survey and is located at the regional office in Salt Lake City, Utah.

V. M. GOLDSCHMIDT, professor of mineralogy and geology at the University of Oslo, has been elected a foreign member of the Royal Society, London.

F. H. KAY and A. C. TROWBRIDGE were the geologists awarded citations as "distinguished alumni" of the college classes prior to 1911 by the University of Chicago.

VICTOR OPPENHEIM was recently elected a member of the Colombian Academy of Science and of the Geological Society of Peru.

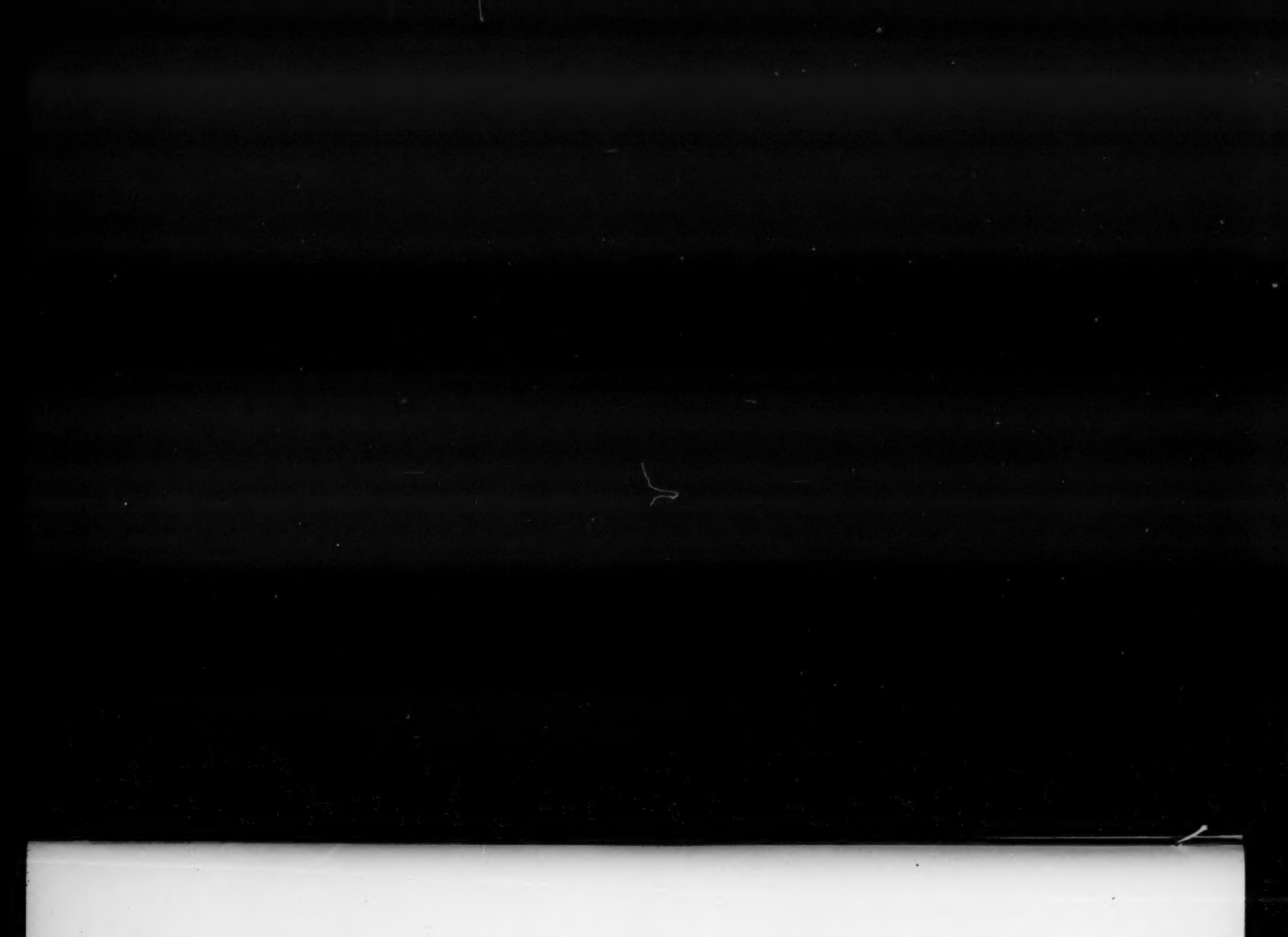
H. G. SCHENCK, professor of geology, is on leave from Stanford University to serve as a major in the Army.

The name of C. S. FOX, director of the Geological Survey of India, appears as a Knight in the Birthday Honors list of the King of England.

W. W. RUBEY is chairman of the Division of Geology and Geography, National Research Council for the year which began July 1. MARLAND BILLINGS and T. S. LOVERING are the G. S. A. representatives to the Council, C. H. BEHRE, JR. is the representative of the S. E. G. and J. T. SINGEWALD, JR. is a member at large.

ARTHUR HOLMES of the University of Durham has been made regius professor of geology and mineralogy at the University of Edinburgh.

As a result of the Mineral Industries Conference last year, sponsored by the Michigan College of Mining and Technology, a well-rounded cooperative program of strategic mineral investigations is being conducted jointly by the U. S. Geological Survey, the Geological Survey division of the Michigan Department of Conservation and several educational institutions of the state. A. K. SNELGROVE, W. A. SEAMAN and V. L. AYRES of Michigan College of Mining and Technology are prospecting for ores of tungsten, molybdenum, beryllium, etc. F. C. PARK, JR. and C. E. DUTTON of the federal and state geological surveys have begun a long-term survey of iron resources. K. K. LANDES and G. M. EHLERS of the University of Michigan department of geology will carry out stratigraphic and structural studies in the Mackinac Straits region.

E. T. HECK, assistant geologist of the West Virginia Geological Survey, has been commissioned Lieutenant (j.g.) in the U. S. Navy; G. E. EDDY of the Michigan Geological Survey has been commissioned First Lieutenant in the Army; R. W. DRIER, assistant professor of geology and mining engineering at Michigan College of Mining and Technology, has been commissioned Lieutenant Commander, U. S. N. R.

K. DE P. WATSON, instructor of economic geology at Princeton University, is now associate mining engineer of the British Columbia Department of Mines.